Reactions of the Sulphur Group Tetrafluorides with Some Rhodium Complexes.

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Acknowledgements.

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To my parents.

Abstract

The complexes $Rh(CO)X(PEt_3)_2$ [X = Cl, Br, I, NCS, NCO] have been reacted with SF_4, SeF_4 and TeF_4 in CD_2Cl_2 and studied by multinuclear n.m.r. spectroscopy.

In each of the the reactions of SF_4 and SeF_4, a range of Rh(III) complexes is formed which contain the SF_3 or novel SeF_3 ligand. Most of these complexes also contain fluorine bonded directly to rhodium and those which do not are believed to be the result of halogen exchange with solvent. The ratios of products in each reaction are dependant upon the size of X in the starting material. The fluxionalities of the MF_3 group [M = S, Se] appears to be dependant upon the size of the ligand which is *trans* to it.

The products of the reactions of $Rh(CO)X(PEt_3)_2$ with TeF_4 similarly produce complexes containing the novel TeF_3 ligand. However, none of these complexes contain fluorine bonded directly to rhodium. Multinuclear n.m.r. spectroscopic data suggest that these complexes are 5 coordinate square pyramidal cations with TeF_5^- as counterion.

List of Abbreviations.

δ	chemical shift/p.p.m.
τ	torr
ϕ	frequency/Hz.
Cp	cyclopentadienyl
Cy	cyclohexyl
Et	ethyl
F.E.P.	tetrafluoroethene/perfluoropropene copolymer
Hz	Hertz
i.d.	inside diameter
Kel-F	polytrifluoroethylene
Me	methyl
N.m.r.	Nuclear magnetic resonance
n.o.	not observed
o.d.	outside diameter
Ph	phenyl
p.p.m.	parts per million
R	alkyl
T	temperature
V.t.	variable temperature
$W_{\frac{1}{2}}$	width at half-height

Contents.

Chapter One

1 Introduction.

This chapter will outline some of the background and chemistry relevant to the work discussed in this thesis.

Oxidative Addition.

Oxidative addition [1-3] is defined as the reaction which occurs when a compound behaves simultaneously as a Lewis acid and as a Lewis base [4] and is generally written as;

$$L_yM^n + XY \longrightarrow L_yM^{n+2}(X)(Y)$$

The reverse reaction is known as *reductive elimination* .

For these reactions to proceed there are three criteria which must be fulfilled;

a) there must be two vacant coordination-sites on the complex L_yM^n to allow formation of the two new bonds to X and Y,

b) there must be non-bonding electron-density on the metal, M, and

c) M must show oxidation states separated by two units.

The definition of oxidative addition extends beyond the boundaries of metal chemistry e.g.;

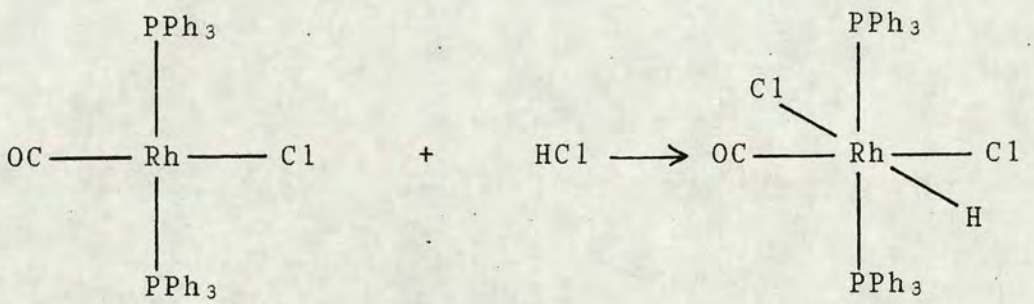
$$TeF_4 + ClF \longrightarrow TeF_5Cl \quad [5]$$

$$PF_3 + Cl_2 \longrightarrow PCl_2F_3 \quad [6]$$

$$ClF_3 + F_2 \xrightarrow{h\nu} ClF_5 \quad [7]$$

However, the oxidative addition reactions which have been studied most are those of transition metal complexes, especially those complexes where the metals have d^8 or d^{10} electronic configurations commonly Fe(0), Ru(0), Os(0), Rh(I), Ir(I), Ni(0), Pd(0), Pt(0) and Pd(II), and Pt(II).

The discovery of Vaska's compound, $Ir(CO)Cl(PPh_3)_2$, led to intense study in this area as the complex was recognised for its importance as a model compound for studies in homogeneous catalysis [8,9]. Vaska's compound and its analogues (the halide can be changed and PPh_3 can be substituted for a variety of other phosphines) were soon discovered to react with H_2, O_2, CH_3I, HX, X_2 [X = Cl, Br & I] and silyl and germyl compounds [8,10-15] e.g.;

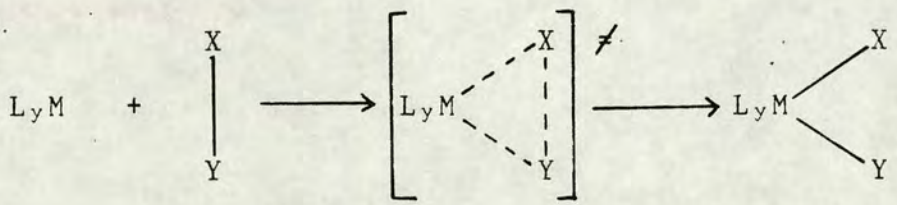


The higher oxidation states are usually more stable for the heavier than for the lighter metals, so that, for example, Ir(III) species are generally more stable than Rh(III) species. Also, on changing, for example, the phosphines in Vaska's compound from PPh_3 to the more basic PEt_3, the Ir(I) complex is more readily oxidised. Steric properties of ligands are also important, as bulky ligands tend to decrease the ease of

oxidative addition. Also, many of the d^6 6 coordinate complexes containing bulky phosphines are only sparingly soluble in most organic solvents, making study by n.m.r. spectroscopy particularly difficult. In the work presented in this thesis we have used triethylphosphine complexes throughout, thus overcoming two obstacles by making the products of oxidative addition more soluble than PPh_3 analogues would be and , by using a more basic phosphine, increasing the likelihood of oxidative addition occurring in the first place.

Stereochemistry of Addition.

When oxidative addition is a concerted process, the addition is necessarily *cis* ;



but when X and Y are separated, the product may be one or more of several isomers. The final product will be the isomer or isomer mixture which is the most stable thermodynamically under the conditions used. The ligands, solvent, temperature, pressure etc. will have a decisive influence on this.

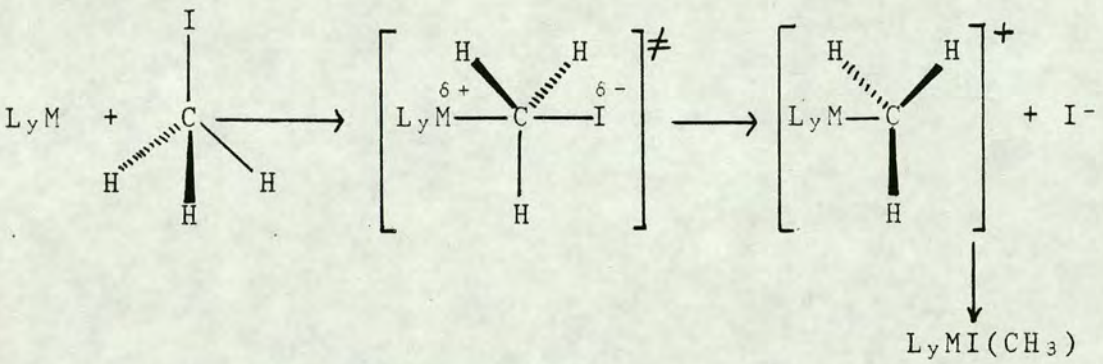
H_2 is believed to add via a concerted, 3-centre addition mechanism to give a *cis* product.

HX is found to add *cis* also if non-polar solvents are used, but if wet or polar solvents are used, *cis-trans* mixtures of products are produced as

the HX molecule will be dissociated.

Organic halides may add by two main mechanisms, S_N2 or radical;

a) In reactions of t-$Ir(CO)Cl(PPh_3)_2$, and analogues, with CH_3I[16] the mechanism is S_N2;



If an optically active halide is used, *inversion* of configuration is observed.

b) Radical pathways, chain or nonchain, have been established in some reactions especially where these are induced by irradiation. The majority of simple bromides and iodides react with Ir(I), Pd(0) and Pt(0) complexes by the chain mechanism although CH_3I seems non-radical. Radical pathways have not been observed for Rh(I).

The extensive studies of oxidative addition which have occurred since the discovery of Vaska's compound have resulted from the need to understand the mechanisms occurring during homogeneous catalysis. The d^8 metal complexes are particularly important [1,3,17,18,19]. Wilkinson's catalyst, $RhCl(PPh_3)_3$, catalyses the hydrogenation of alkenes under mild conditions[20] and $Rh(CO)H(PPh_3)_3$ catalyses the

hydroformylation of alkenes[21]. The initial step in both of these processes is the oxidative addition of dihydrogen.

The Sulphur Group Tetrafluorides.

SF_4.

Sulphur tetrafluoride was first isolated and characterised in 1950[22] and since 1954 its structure and reactivity have been the subject of intensive study. The discovery that SF_4 is a unique and specific fluorinating agent has been of particular value in synthetic work.

Sulphur tetrafluoride is prepared by the reaction of SCl_2 with NaF in acetonitrile[22]. Once prepared it is conveniently stored in stainless-steel cylinders or at low temperature in pyrex equipment which has been scrupulously dried beforehand.

At room temperature sulphur tetrafluoride has a vapour pressure of ~10 atmospheres, making it an ideal reagent for manipulating in a pyrex vacuum line.

The structure of sulphur tetrafluoride is trigonal bipyramidal in which two fluorine atoms and the unshared electron pair occupy the equatorial positions and the other two fluorine atoms are in the axial positions. There is a significant difference between the (long)SF_{ax} and (short)SF_{eq} distances. This has been rationalised on the basis of a charge-transfer configuration via $sp_xp_y + p_z$ with the p_z orbital on sulphur being involved in a 3-centre 4-electron bond with the two axial fluorine atoms[24].

Sulphur tetrafluoride is unusual in apparently acting both as an electron-pair donor and an electron-pair acceptor[25] such that pyridine forms a 1:1 adduct, $C_5H_5NSF_4$. Likewise CsF forms CsF_5. By contrast, SF_4 behaves as a donor to form 1:1 adducts with Lewis acids. It is likely that here SF_4 is acting, not as a sulphur lone-pair donor but as a fluoride ion lone-pair donor and, indeed, infra-red spectroscopy suggests that $SF_4.BF_3$ is predominantly $[SF_3^+][BF_4^-]$.

The selective replacement of oxygen and sulphur atoms by fluorine in many types of organic compounds has been shown to be a general and particularly useful reaction of sulphur tetrafluoride. It is a remarkably effective reagent for the selective replacement of carbonyl oxygen by fluorine in a wide range of organic compounds;

$$>C{=}O \quad + \quad SF_4 \longrightarrow >CF_2 \quad + \quad SOF_2$$

e.g.;

$$CH{\equiv}CCOOH \quad + \quad SF_4 \longrightarrow CH{\equiv}CCF_3 \text{ [26]}$$

$$ArO\overset{\overset{O}{\|}}{C}F \quad + \quad SF_4 \xrightarrow{HF} ArOCF_3 \text{ [27]}$$

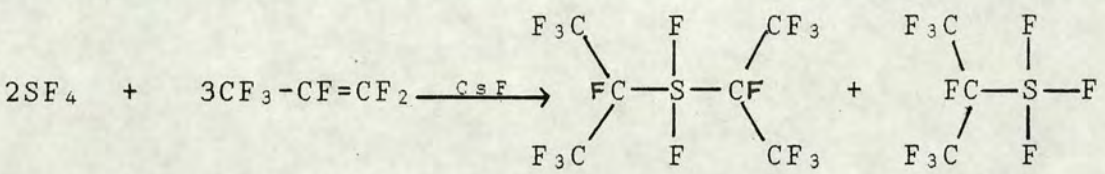
$$C_6H_5CHO \quad + \quad SF_4 \longrightarrow C_6H_5CHF_2 \text{ [26]}$$

Sulphur tetrafluoride is a versatile reagent for preparing a wide range of inorganic fluorides by replacement of oxygen or sulphur in inorganic compounds[28]. Examples of binary fluorides prepared from oxides and SF_4 include UF_6, WF_6, IF_5, SeF_4, TeF_4 and GeF_4 e.g.;

$$I_2O_5 + 5SF_4 \longrightarrow 2IF_5 + 5SOF_2$$

The synthesis of ternary fluorides based on SF_4 reactions leads to an effective route to inorganic fluorides[29,30] e.g. $NaNbF_6$, Na_2WF_8, $CsWF_6$ and $TlMoF_6$.

Sulphur tetrafluoride has also been used in the preparation of tetracoordinate perfluoroalkyl sulphur(IV) fluorides[31,32];



$$SF_4 + Et_2N\text{-}SiMe_3 \longrightarrow Et_2NSF_3 + FSiMe_3$$

^{19}F n.m.r. spectroscopy is an ideal technique for investigating these complexes, their reactions and exchange processes.

<u>SeF_4.</u>

Selenium tetrafluoride is a white, hygroscopic, crystalline solid melting at -9.5°C to a colourless liquid. It is made by heating SeO_2 with SF_4 at high pressure[33]. Even when dry selenium tetrafluoride attacks glass. The structure is trigonal bipyramidal with two fluorines and the lone pair of electrons in the equatorial positions and the other two fluorines in the axial positions, as in SF_4[34,35]. Selenium tetrafluoride forms adducts with Lewis acids and Lewis bases e.g.;

$$SeF_4 + BF_3 \longrightarrow [SeF_3^+][BF_4^-]$$

$$SeF_4 + NO_2F \longrightarrow [NO_2][SeF_5^-]$$

Selenium tetrafluoride is a useful fluorinating agent. Water hydrolyses it violently and the compound dissolves bromine, iodine, selenium, sulphur and tellurium dioxide. It is reduced to selenium by arsine, hydrogen selenide and sulphide and by potassium iodide, but it reacts with potassium bromide to form the appropriate selenium tetrahalide.

TeF_4.

Tellurium tetrafluoride is a white, hygroscopic crystalline solid which melts at 129°C. It is prepared by reaction of SF_4 and TeO_2 at high temperature and pressure[36]. The compound is readily hydrolysed but can safely be handled in dry glassware. Tellurium tetrafluoride behaves much as does its selenium analogue but appears to be less useful as a fluorinating agent. The structure is a polymeric chain built up by sharing *cis* fluorine atoms between square pyramidal TeF_5 units. It forms 1:1 adducts with Lewis acids such as BF_3 and SbF_5. A few metal salts of the pentafluorotellurate(IV) ion have been reported[37,38], but these have not been synthesised from TeF_4. None of these salts is stable.

Reactions of Transition-Metal Complexes with Inorganic Fluorides.

In spite of the comprehensive investigations into transition-metal chemistry over the past thirty years there has only been a handful of transition-metal fluoride complexes prepared.

This is not because of any inherent instability

of these species but because fluorinations have traditionally been carried out directly with elemental fluorine or halogen fluorides which tend to be destructive. Recently, new approaches using inorganic fluorides dissolved in suitable inert solvents have resulted in the characterisation of a new range of transition-metal compounds.

During the last several years studies have been carried out on the reactions of main-group element binary fluorides such as NF_3, AsF_3, XeF_2 and SF_4 with transition-metal complexes of the type $[M(CO)X(PEt_3)_2]$ [M = Rh, Ir; X = Cl, Br, I]. The reactions have yielded interesting and novel products. For example, XeF_2 has been observed to fluorinate certain main-group ligands attached to coordinatively saturated metal centres[39,40];

$$Ir(CO)Cl_2(PEt_3)_2PF_2 \longrightarrow Ir(CO)Cl_2(PEt_3)_2PF_4$$

$$Ir(CO)BrH(PEt_3)_2PH_2 \longrightarrow Ir(CO)Br(PEt_3)_2PF_2H_2$$

and fluorination of main-group element ligands attached to coordinatively unsaturated metal centres is also possible where we see the elements of F_2 added across an Ir-C bond and oxidation of Ir(I) to Ir(III)[41];

$$[Ir(CO)_3(PEt_3)_2^+] \xrightarrow{XeF_2} [Ir(CO)_2(COF)F(PEt_3)_2]$$

Some rather stable fluorides such as NF_2Cl and SF_4 have also been observed to undergo oxidative addition reactions and, in the case of the SF_4 reaction

the metal centre was inserted into a S-F bond[42,43];

$$M(CO)Cl(PEt_3)_2 + NF_2Cl \longrightarrow M(CO)Cl_2(PEt_3)_2NF_2 \quad [M = Rh, Ir]$$

$$Ir(CO)Cl(PEt_3)_2 + SF_4 \longrightarrow Ir(CO)ClF(PEt_3)_2SF_3$$

These reactions suggest that there may be a significant new chemistry to be discovered in the area of reactions of inorganic fluorides with transition-metal complexes.

N.m.r. Spectroscopy.

Nuclear magnetic resonance spectroscopy is the technique used almost entirely throughout this thesis. The theory behind n.m.r. and its practical applications have been discussed at length in various texts and reviews[44-46]. Two relatively uncommon n.m.r. techniques were used during the work described in this thesis namely ^{19}F-^{19}F COSY n.m.r.[44] and ^{19}F-{^{19}F} n.m.r. spectroscopy[45].

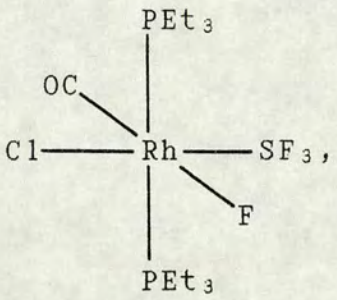
COSY is an acronym for COrrelation SpectroscopY and involves applying a second pulse of radio frequency to a system which already has some transverse magnetisation. This pulse causes magnetisation which arose from one transition during t_1 to be redistributed amongst all the others with which it is associated. This produces a 2D n.m.r. spectrum with the 1D spectrum observed along the diagonal and off-diagonal peaks are observed between all lines which are either part of the same multiplet or parts of different multiplets which

share a coupling.

The simplest double resonance experiment is the coherent irradiation of one multiplet. In the rotating frame the equilibrium magnetisation is along the z-axis; the addition of resonant radio frequency causes rapid precession of the vectors of that part of the spin multiplet about the x-axis. This precession has the effect, as viewed from the other part of the spin multiplet of averaging away the splittings caused by spin coupling. In order to achieve complete spin decoupling, the decoupling field (B_2) must be powerful enough to affect all the components of the spin multiplet equally, i.e. $\gamma B_2 >> \Sigma nJ$ (γ= magnetogyric ratio). If lower powers are used, more complex spectra are observed.

Chapter Two.

Key to Structures and Numbers in Chapters 2 & 3



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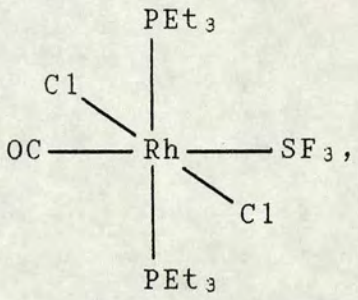

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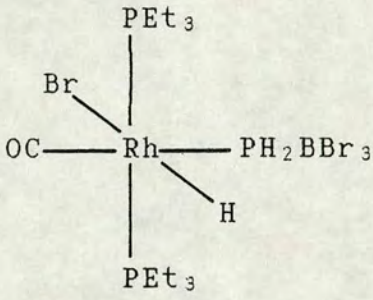

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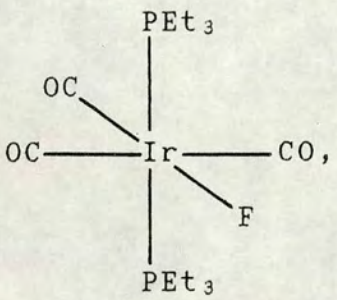

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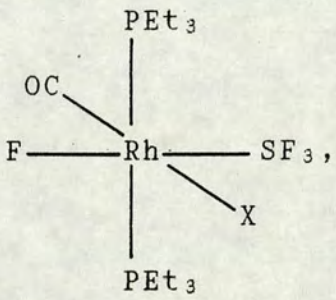

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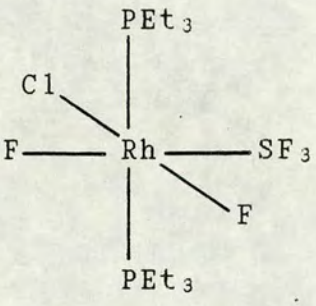

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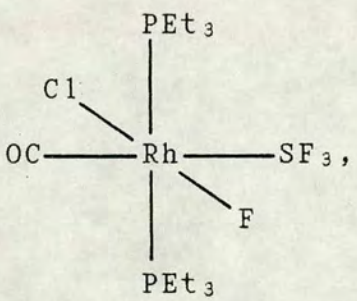

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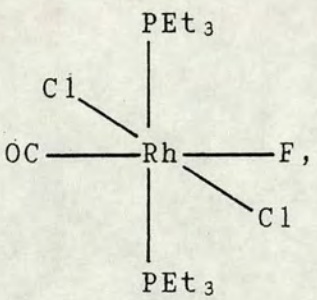

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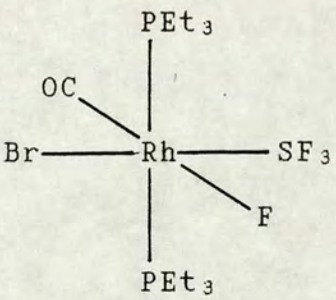

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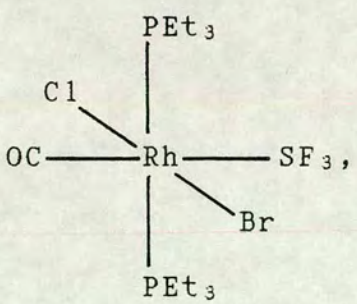

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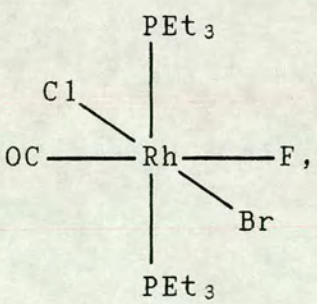

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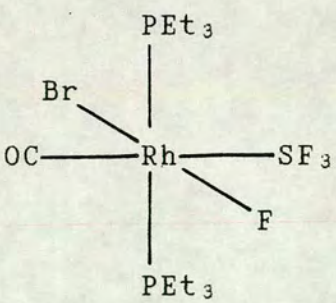

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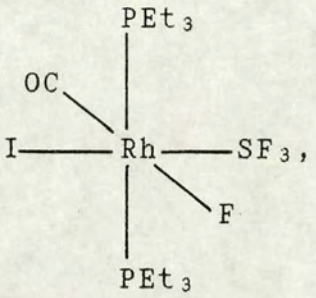

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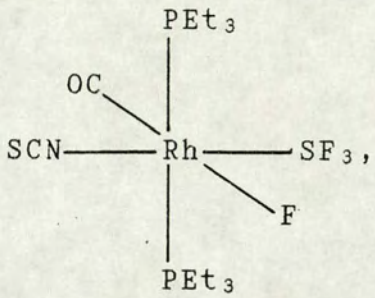

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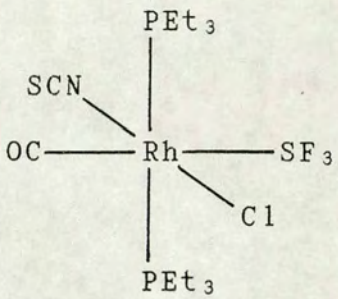

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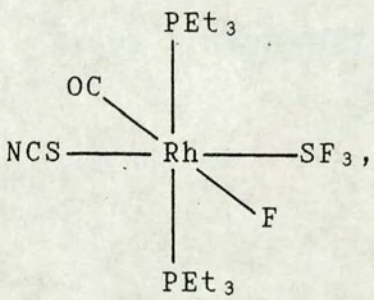

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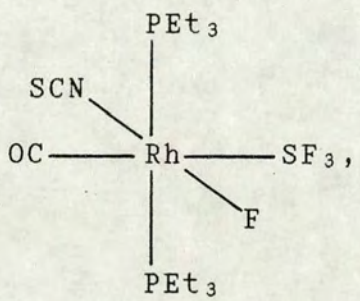

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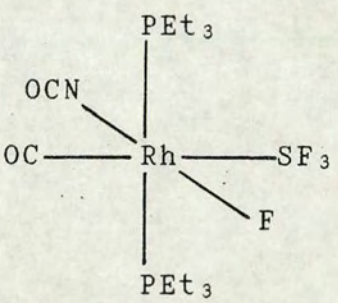

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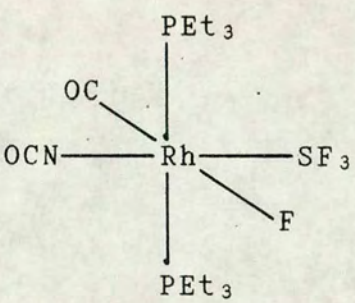


[XIX]

Summary

The reaction between $Rh(CO)Cl(PEt_3)_2$ and SF_4 occurred rapidly in CD_2Cl_2 at 195K to give a clean sample of $Rh(CO)ClF(PEt_3)_2SF_3$.

At 195K the $^{19}F-\{^1H\}$ n.m.r. spectrum showed several complicated resonances which we have assigned as arising from four different 6-coordinate $Rh(III)-SF_3$ complexes.

There was one major product, [I], which was analogous to that formed in the reaction of $Ir(CO)Cl(PEt_3)_2$ with SF_4[43], and three significantly less abundant complexes; one was the *trans* dichloride complex, [II], one was identified as the *cis* difluoride SF_3 complex, [VI], and the third as the isomer of the major product, [I], with CO trans to the SF_3 group [VII].

2.1 Reaction of $Rh(CO)Cl(PEt_3)_2$ and SF_4.

The reaction between $Rh(CO)Cl(PEt_3)_2$ and SF_4 was followed by $^{19}F-\{^1H\}$ n.m.r. spectroscopy [figure 2.1.1]. On melting, the solution became claret coloured. Four resonances, F_A, $F_{A'}$, F_E and F_M were observed with approximately equal intensity. The lowest frequency resonance, F_M, was a doublet of triplets of narrow doublets at δ-357.8, a region associated with F bonded directly to a Rh(III) centre [47]. The remaining three resonances were all in a region associated with F bonded directly to S[48]: a doublet of doublets of doublets of narrow triplets at δ-73.5, a doublet of doublets of doublets of doublets of doublets at δ45.6 and a doublet of doublets of doublets of doublets at δ76.8.

These positions and splittings were analogous to those observed for the Ir-SF_3 complex but each multiplet showed one additional doublet splitting which arose from coupling to ^{103}Rh. These ^{103}Rh-F couplings (115Hz for the low frequency fluoride and ~15Hz for the other three) are consistent with 1-bond and 2-bond couplings respectively[48]. Expansions of all four resonances are given in figures 2.1.2 and 2.1.3 and parameters detailed in tables 2.1.1 and 2.1.2.

Table 2.1.1. Chemical Shifts for Species [I]

S-F		Rh-F		P	
F_A	$F_{A'}$	F_E	F_M	P_A	P_B
76.8	45.6	-73.5	-357.8	33.8	27.5

Figure 2.1.1; $^{19}F - \{^{1}H\}$ n.m.r. spectrum of $Rh(CO)Cl(PEt_3)_2 + SF_4$ at 195 K

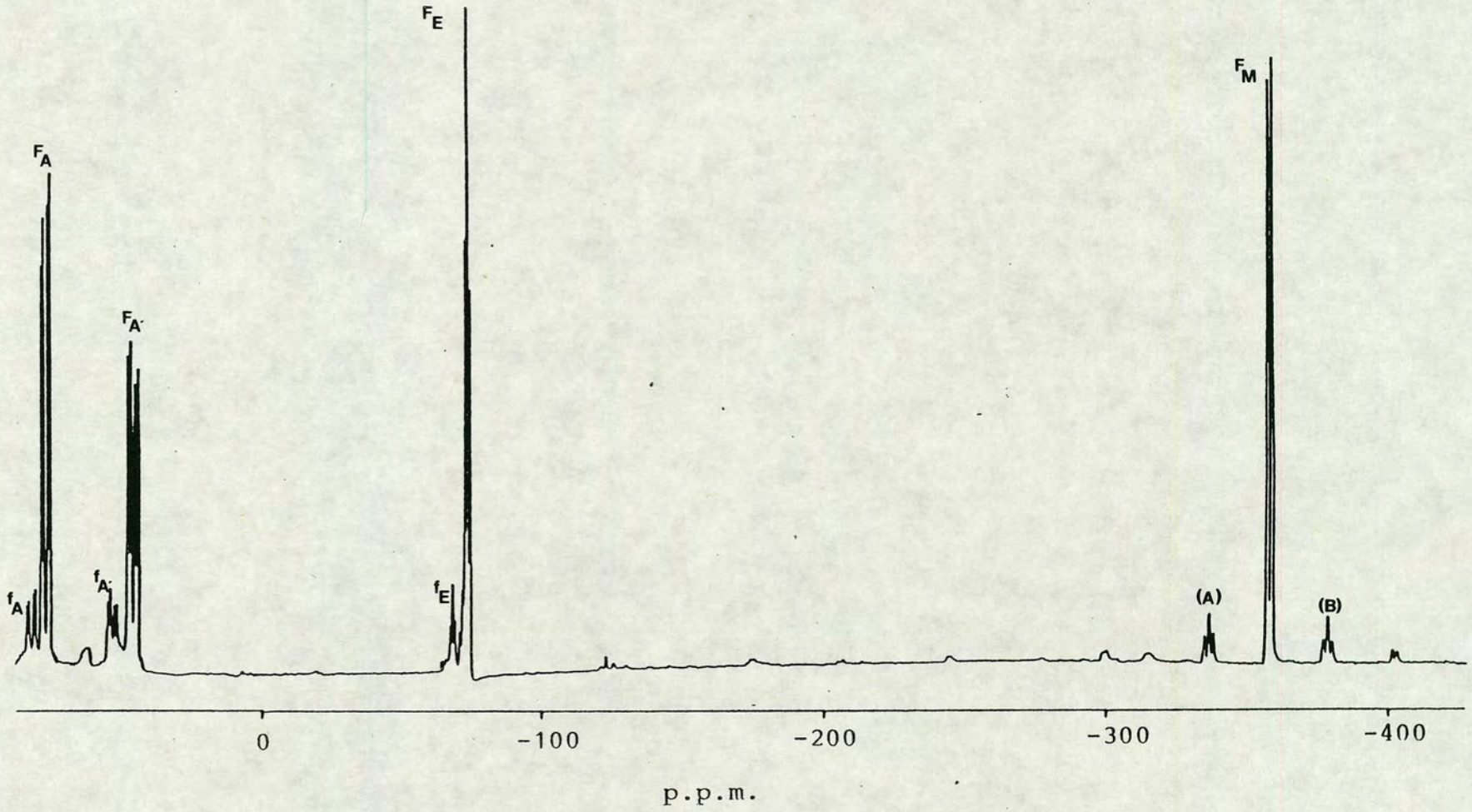
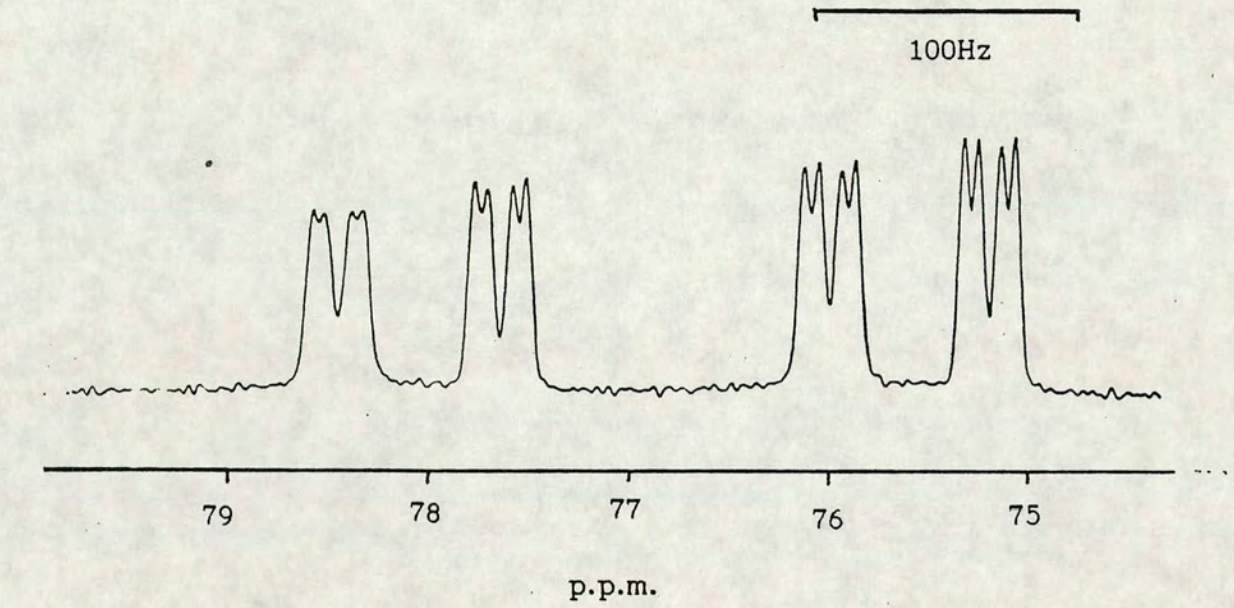


Figure 2.1.2; Expansions of F_A & $F_{A'}$



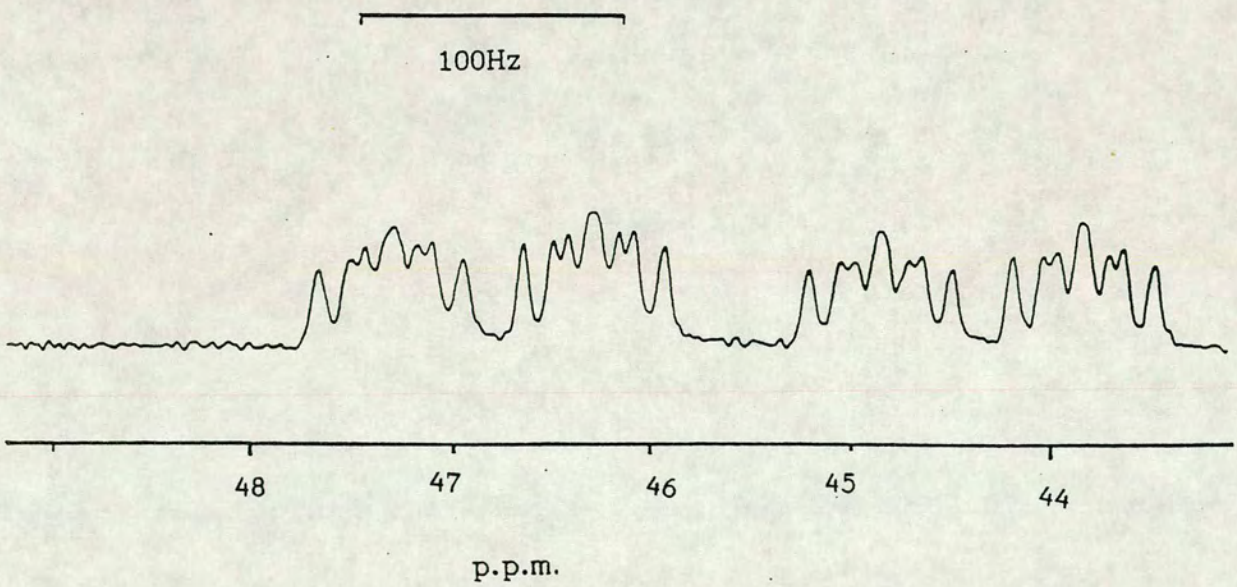
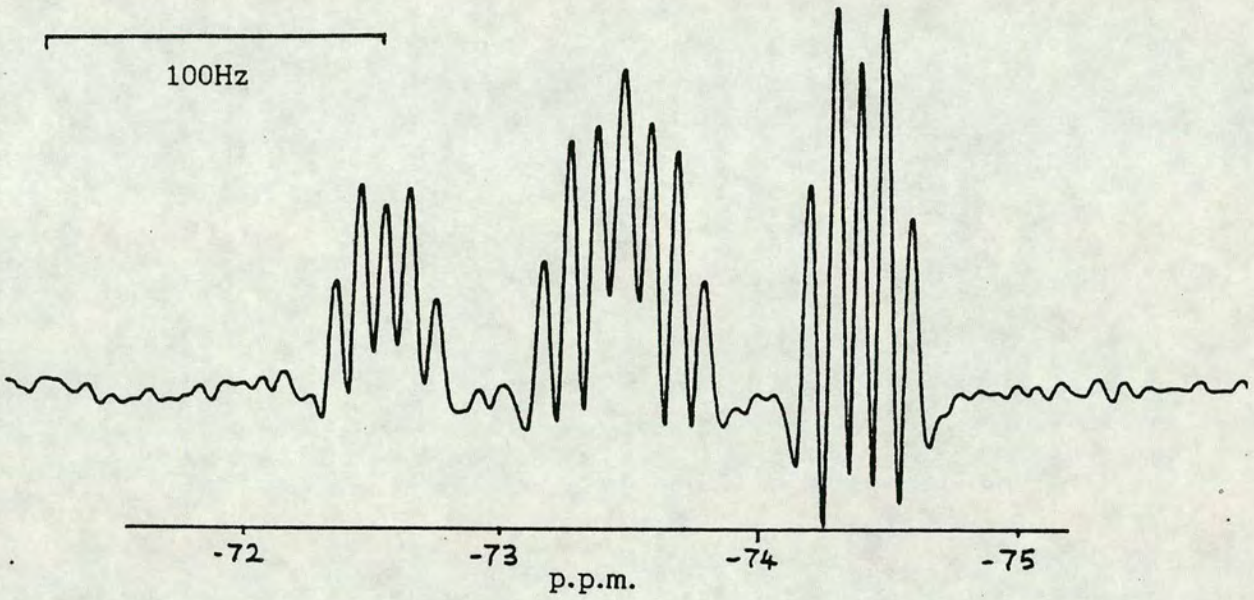


Figure 2.1.3; Expansions of F_E & F_M



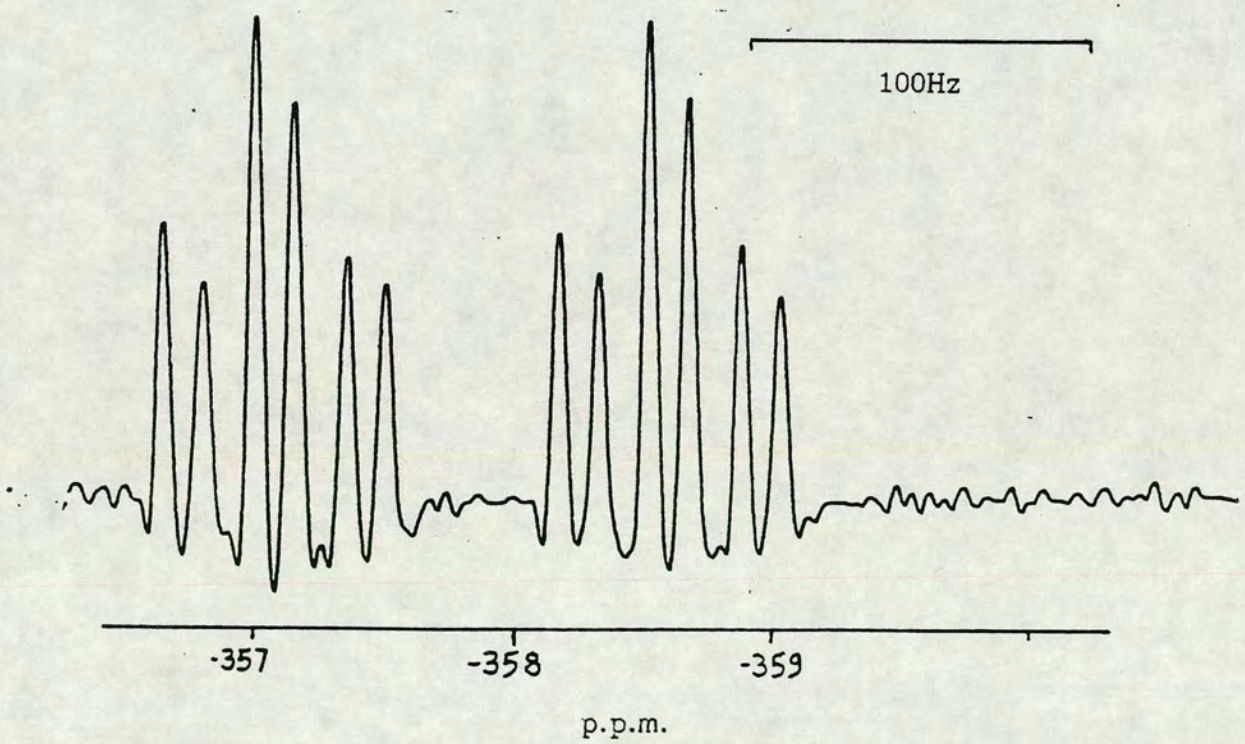
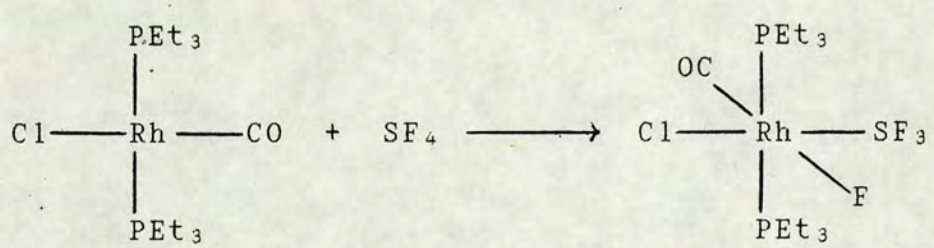


Table 2.1.2. Coupling Constants for Species [I]

Nuc.	F_A	$F_{A'}$	F_E	F_M	P_A	P_B	Rh
F_A	-	186	60	n.o.	n.o.	5	14
$F_{A'}$	186	-	77	12	25	n.o.	17
F_E	60	77	-	n.o.	8	8	14
F_M	n.o.	12	n.o.	-	26	26	115
P_A	n.o.	25	8	26	-	420	78
P_B	5	n.o.	8	26	420	-	78

Thus it was assumed that oxidative addition of SF_4 had occurred as in the analogous Ir system; [figure 2.1.4]

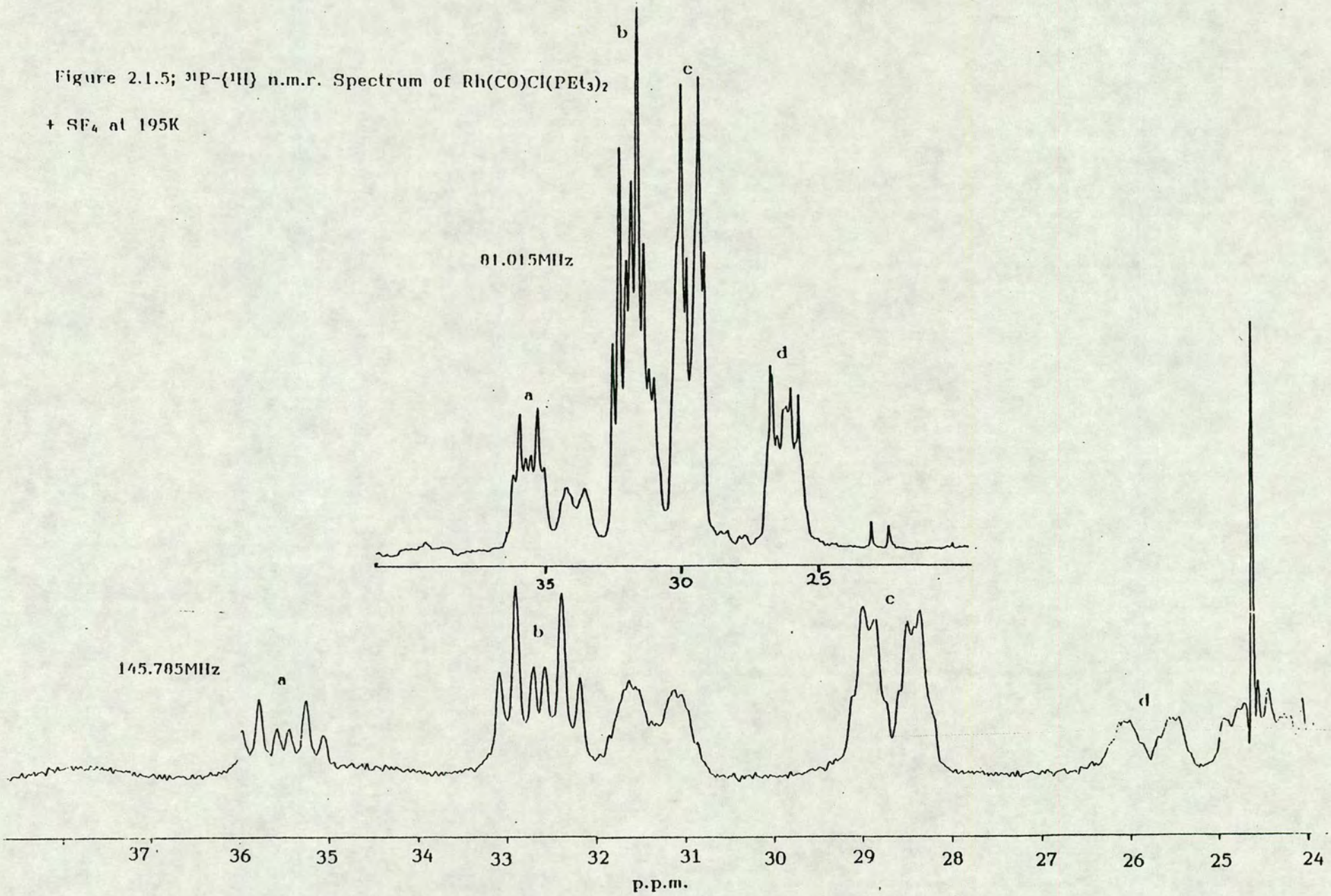


[I]

The 145.785MHz $^{31}P-\{^1H\}$ n.m.r. spectrum at 195K [figure 2.1.5] supported this conclusion, showing an ABQRSTX pattern. In this pattern, J_{AB} could readily be identified ($^2J_{AB}$ = 420Hz); there appeared to be a second doublet splitting of 78Hz, consistent with a 1-bond P-Rh(III) coupling[47] with further splitting in both the A and B components, interpreted as arising from coupling to four inequivalent F atoms.

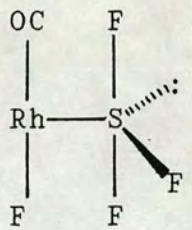
The phosphorus nuclei are magnetically inequivalent due to asymmetry at sulphur, whose coordination positions are occupied by rhodium, by three

Figure 2.1.5; $^{31}P-\{^{1}H\}$ n.m.r. Spectrum of $Rh(CO)Cl(PEt_3)_2$ + SF_4 at 195K



chemically distinct fluorine atoms and by a lone pair of electrons;

[figure 2.1.6]



The ^{31}P chemical shifts for these two phosphorus atoms must be calculated from the positions of the four multiplets which form the basic AB pattern[49].

From the $^{31}P-\{^{1}H\}$ n.m.r. spectrum [figure 2.1.5], the frequencies of the four multiplets a, b, c and d were measured. The positions of these multiplets are given by:

$$a = \tfrac{1}{2}(\phi_A + \phi_B) - \tfrac{1}{2}J - \tfrac{1}{2}D$$

$$b = \tfrac{1}{2}(\phi_A + \phi_B) + \tfrac{1}{2}J - \tfrac{1}{2}D$$

$$c = \tfrac{1}{2}(\phi_A + \phi_B) - \tfrac{1}{2}J + \tfrac{1}{2}D$$

$$d = \tfrac{1}{2}(\phi_A + \phi_B) + \tfrac{1}{2}J + \tfrac{1}{2}D$$

where ϕ_A = frequency of P_A, ϕ_B= frequency of P_B

$$J = \phi_b - \phi_a = \phi_d - \phi_c,\ D = \phi_B - \phi_A$$

$$D^2 = [(\phi_A - \phi_B)^2 + J^2]$$

now,

$$\tfrac{1}{2}(\phi_A + \phi_B) - \tfrac{1}{2}J - \tfrac{1}{2}D = 5180$$

$$\tfrac{1}{2}(\phi_A + \phi_B) + \tfrac{1}{2}J + \tfrac{1}{2}D = 3760$$

$$(\phi_A + \phi_B) = 8940\text{Hz} \quad \text{and,}$$

$$\tfrac{1}{2}(\phi_A + \phi_B) + \tfrac{1}{2}J + \tfrac{1}{2}D = 3760$$

$$\tfrac{1}{2}(\phi_A + \phi_B) - \tfrac{1}{2}J - \tfrac{1}{2}D = 5180$$

$$J + D = -1420\text{Hz}$$

from the spectrum, $J = 420\text{Hz}$

$D = -1000\text{Hz}$ (sign is irrelevant)

$D^2 = [(\phi_A - \phi_B)^2 + J^2]$

$\therefore \phi_A - \phi_B = \pm 910\text{Hz}$,

$\phi_A + \phi_B = 8940\text{Hz}$

$\therefore \phi_A = 4015$ or 4925Hz

If $\phi_A = 4925\text{Hz}$ then $\phi_B = 4015\text{Hz}$

$\therefore P_A = \delta 33.8$ and $P_B = \delta 27.5$

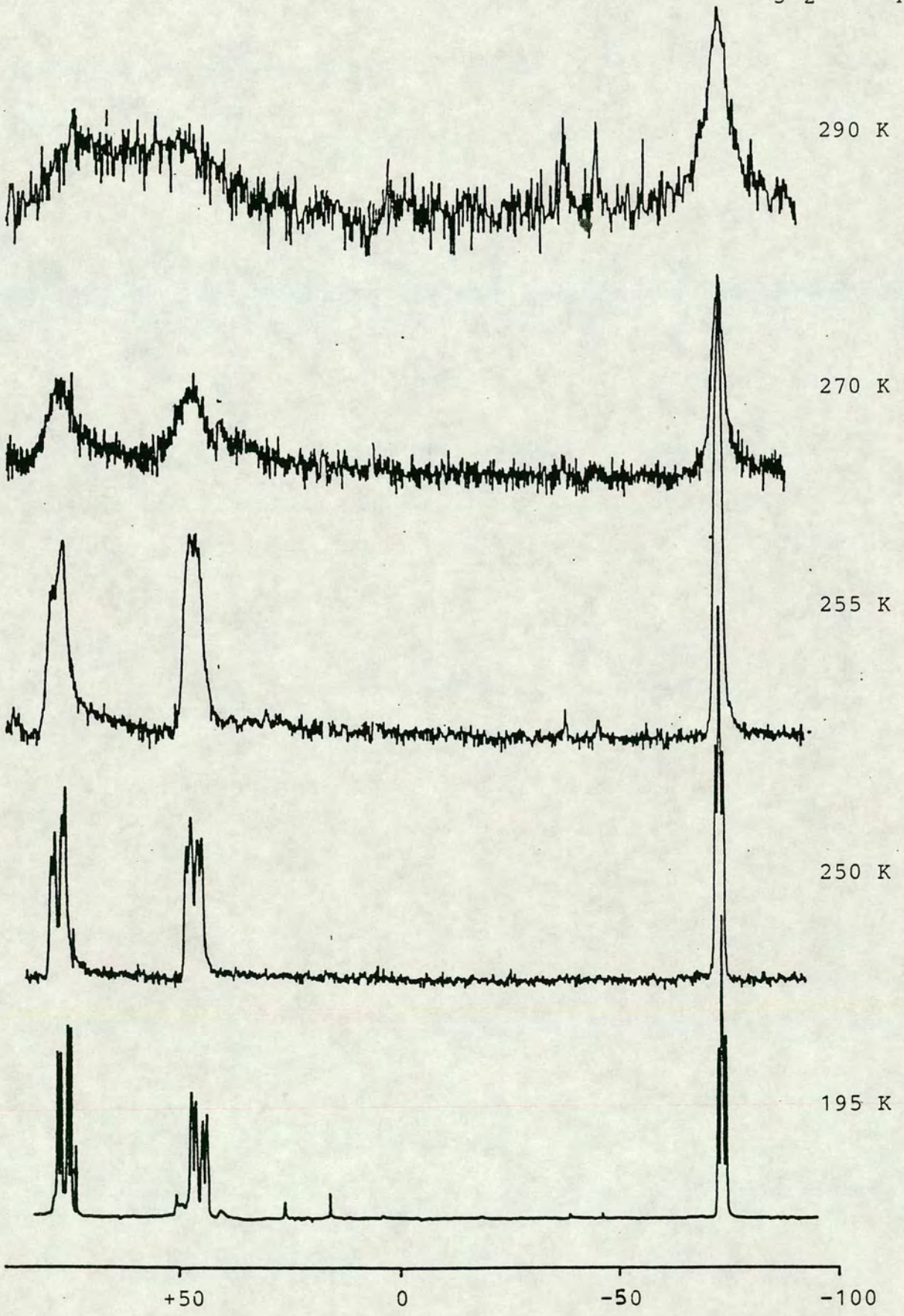
These chemical shifts are consistent with PR_3 bonded to a Rh(III) centre[50].

On warming, the $^{19}F-\{^1H\}$ n.m.r. spectrum changed [figure 2.1.7]. At 250K, the two high frequency S-F resonances began to broaden, although the equatorial S-F and Rh-F resonances remained sharp.

At 255K the two axial S-F resonances had broadened so much that only their mutual coupling could be observed. The equatorial S-F resonance had, at this temperature, begun to show signs of broadening but the Rh-F resonance still remained sharp.

At 270K both axial S-F resonances had broadened

Figure 2.1.7; V.t. ^{19}F n.m.r. spectra of $Rh(CO)Cl(PEt_3)_2 + SF_4$



and lost all couplings. The equatorial S-F had also lost all couplings but the Rh-F resonance had sharpened to a doublet of triplets, losing its coupling to the axial S-F.

On further warming to 290K the only change observed was that the axial S-F resonances became broader.

On recooling to 195K from 290K, the four resonances resharpened and the initial spectrum was once again observed, indicating that the fluxional process was reversible.

If the solution was heated to 295K the two axial S-F resonances were observed to coalesce to a single resonance with the equatorial S-F broadening. However, decomposition also occurs at this temperature.

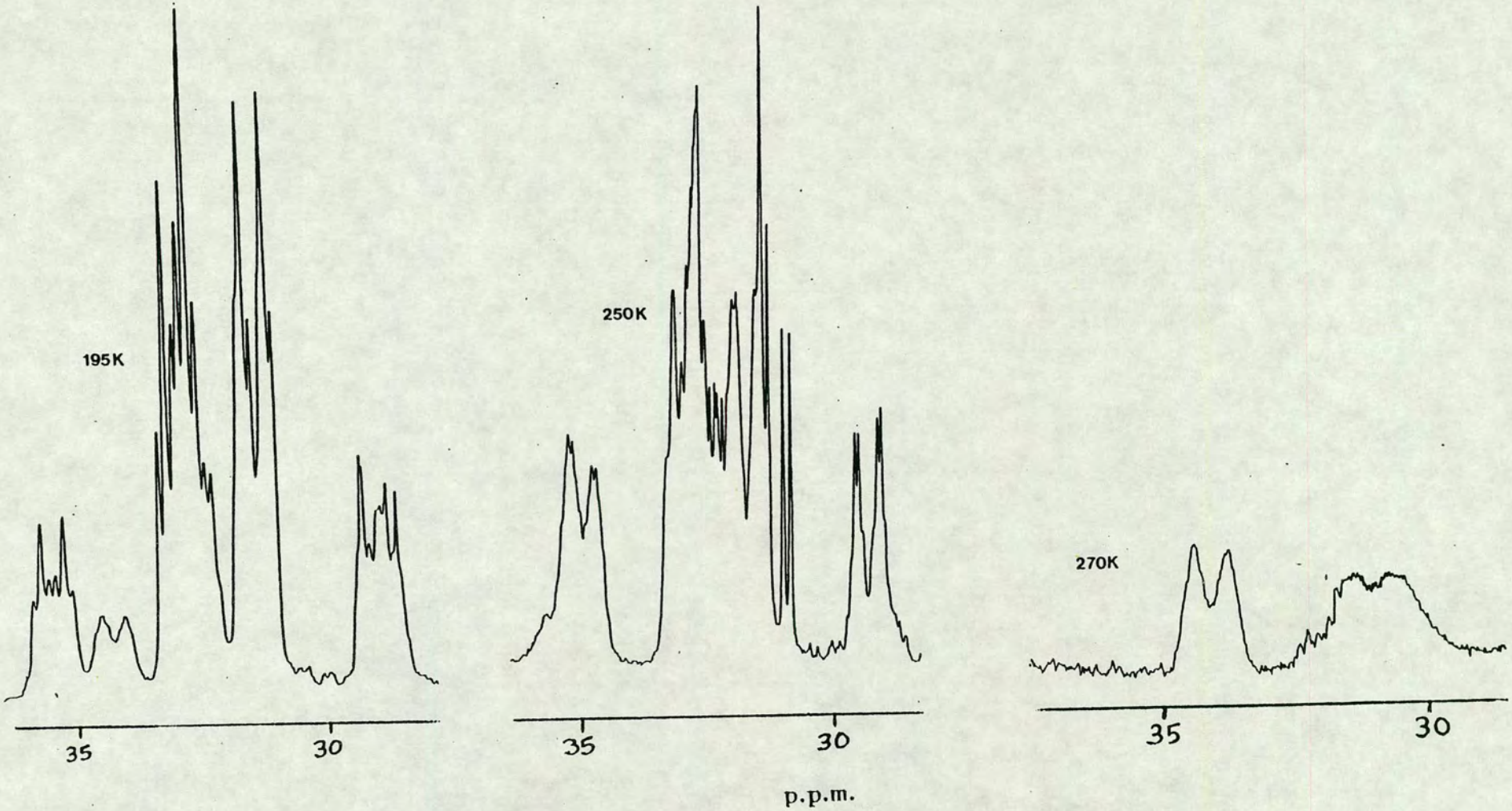
The changes in the S-F resonances on warming indicate that a fluxional process becomes successively faster so that at 295K the two axial S-F's become equivalent, while the equatorial S-F remains distinct.

Observing the $^{31}P-\{^{1}H\}$ n.m.r. spectrum on warming [figure 2.1.8] showed all four parts of the AB pattern beginning to lose their couplings at 250K and at 270K a very broad resonance was observed; it appeared to be a doublet but the spectrum was difficult to interpret due to the imposition of resonances due to decomposition products.

When the tube was recooled from 295K to 195K, the $^{19}F-\{^{1}H\}$ n.m.r. spectrum had changed quite dramatically. In addition to the resonances due to

Figure 2.1.8; V.t. $^{31}P-\{^{1}H\}$ n.m.r. Spectra of $Rh(CO)Cl(PEt_3)_2 + SF_4$

145.785MHz

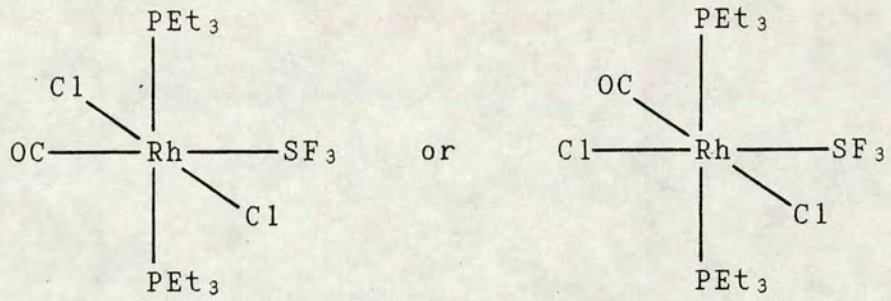


species [I] which were still very prominent, peaks due to several decomposition products were observed. These will be discussed later.

The most significant features in the $^{19}F-\{^{1}H\}$ n.m.r. spectrum at this temperature, however, apart from the resonances attributed to [I], were three other resonances, f_A, $f_{A'}$ and f_E of approximately equal intensity lying slightly to high frequency of the corresponding resonances of [I], each being approximately 20% of the intensity of the corresponding resonance of [I]. They appeared as a doublet of doublets of doublets of doublets at δ82.8, a doublet of doublets of doublets of doublets at δ52.8 and a doublet of doublets of doublets of narrow triplets at δ-68.3. Parameters are detailed in tables 2.1.3 and 2.1.4. Since these three resonances lay in positions very similar to those of the SF_3 group of [I] they were assigned to another SF_3 complex of rhodium. There was, however, no associated Rh-F resonance detected in the $^{19}F-\{^{1}H\}$ n.m.r. spectrum.

These resonances all had the same multiplicities as those of [I], except for the low frequency axial S-F resonance which did not show the coupling to Rh-F observed in the analogous resonance of [I]. This led us to identify this complex, [II], as either;

[figure 2.1.9]



[II]M [II]N

In an attempt to elucidate the correct stereochemistry of this complex, the starting material enriched with 90% ^{13}C in the carbonyl group [$Rh(^{13}CO)Cl(PEt_3)_2$] was prepared and allowed to react with SF_4 as before. The $^{19}F-\{^1H\}$ n.m.r. spectrum observed at 195K differed from that of the reaction of the unenriched starting material with SF_4 in only two respects;

i) the highest frequency resonance of [II] now showed an extra doublet coupling of J = 25Hz [figure 2.1.10] and

ii) the Rh-F resonance of [I] showed an extra doublet coupling of J = 77Hz [figure 2.1.11].

These results have been interpreted as follows.

Generally, in simple octahedral transition metal complexes, a *trans* X-Y coupling constant is around ten times the magnitude of a *cis* X-Y coupling constant[51].

e.g. in the species;[50]

Figure 2.1.10; Expansion of f_A

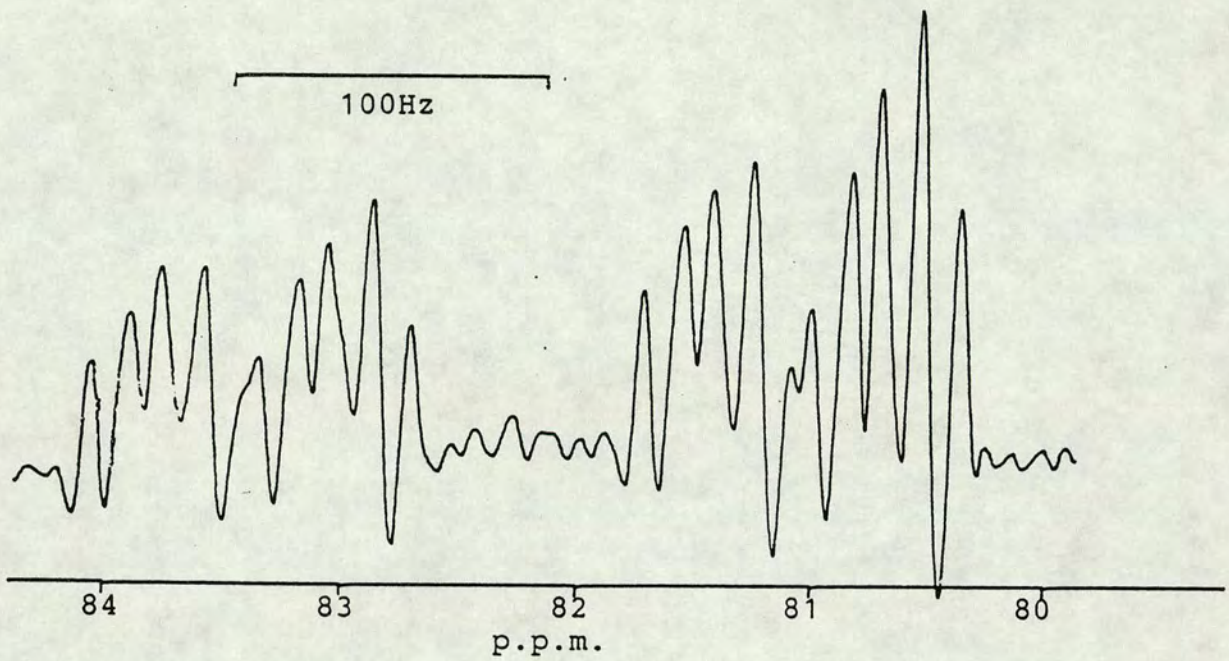
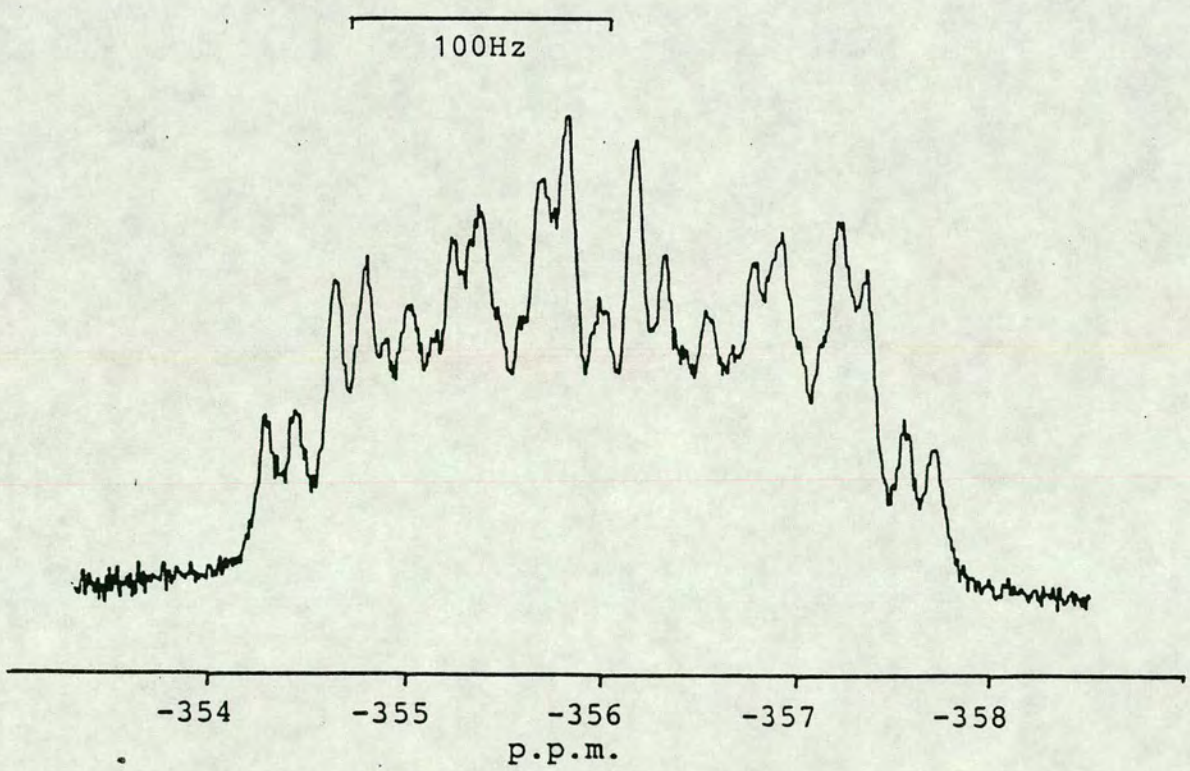
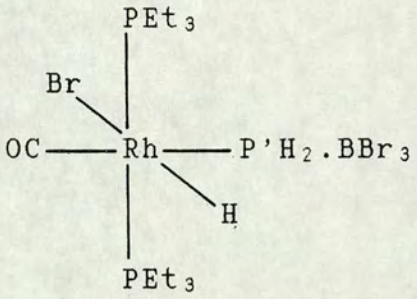


Figure 2.1.11; Expansion of F_M



[figure 2.1.12]



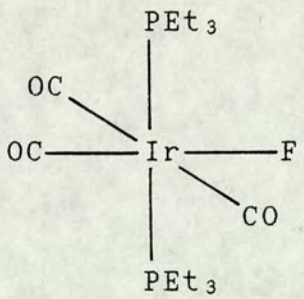
[III]

trans $^{2}J_{C-P}$ = 110Hz and

cis $^{2}J_{C-P}$ = 13Hz.

and in the fluorine containing species;[41]

[figure 2.1.13]



[IV]

trans $^{2}J_{F-C}$ = 62Hz and

cis $^{2}J_{F-C}$ = 7Hz.

On this basis we have assigned the 77Hz coupling in the Rh-F resonance as arising from $^{2}J_{C-F}$ (*trans*) confirming that the geometry of [I] is the same as in the analogous iridium complex.

Also, an n-bond coupling constant is often around ten times larger than an (n+1)-bond coupling constant,

e.g. in complex [I]

$^{1}J_{F-Rh}$ = 115Hz and

$^{2}J_{F-Rh}$ = 15Hz.

This generalisation however, becomes more difficult to apply when one goes from two to three bond couplings, especially where non-orthogonal bond angles are important. Nevertheless, the $^{3}J_{F-C}$ coupling observed in [II] is too large to be *cis* , so we have assigned it as arising from $^{3}J_{C-F}$(*trans*).

As a result, we have assigned structure M. to [II].

It was difficult to assign the ^{31}P n.m.r resonance for this complex as the spectrum recorded at 81.015MHz, although generally well resolved, had several resonances superimposed upon each other. A problem with the ^{31}P n.m.r. spectra of PEt_3 complexes is that the chemical shift range of the phosphorus nuclei is very small; even comparing Rh(I) and Rh(III) complexes one observes a δ range of around 20 p.p.m., and since the ABQRSTX pattern of species [I] itself spans 11 p.p.m., assignment of the spectrum of complexes present in low abundance is particularly difficult.

The spectrum recorded at 145.785MHz was more spread out but chemical shift anisotropy[45] caused loss of resolution. However, we can obtain useful information by comparing the spectra recorded at two different frequencies.

In the 145.785MHz $^{31}P-\{^{1}H\}$ n.m.r. spectrum recorded at 195K, a multiplet, m, was observed at δ31.4 [figure 2.1.5]. This is within the region expected for PR_3 bound to Rh and also appeared to be the correct relative intensity for the PEt_3 groups of [II]. The only coupling we could resolve was the doublet $^{1}J_{P-Rh}$ (74Hz). Thus we assigned this resonance as arising from the triethylphosphine groups of [II]. In the 81.02MHz ^{31}P n.m.r. spectrum we could not detect this resonance as it lay underneath the b and c multiplets of the ABQRSTX pattern of [I] [figure 2.1.5].

On warming the solution, we again observed changes in the $^{19}F-\{^{1}H\}$ n.m.r. spectrum which were consistent with fluxional behaviour.

At 220K the ^{19}F n.m.r. resonances of the two axial SF resonances of [II] began to lose their structure (c.f. 250K for [I]) while the equatorial S-F resonance remained sharp. At 230K both axial S-F resonances now only showed their mutual coupling and the equatorial S-F resonance began to broaden.

On further warming to 240K, the axial S-F resonances could only be observed as broad shoulders on the sides of the still sharp axial S-F resonances of [I]. The equatorial S-F resonance had by now lost all its couplings.

By 250K the equatorial S-F resonance began to broaden and merge with the equatorial S-F resonance of [I]. A new resonance was observed in the axial S-F

region. This was a broad, unresolved peak at δ65.5 ($W_{½}$ = 250Hz). The ratio of the intensity of this resonance to that of the axial SF's of [I] was roughly twice as large as that of the equatorial S-F resonance of [II] at 220K to the axial S-F resonances of [I]. Since the expected position for a coalesced resonance of f_A and $f_{A'}$ would be 67.8 p.p.m., assuming no change in chemical shift due to temperature, we have assigned this new resonance as being due to a pair of equivalent axial S-F resonances.

At 255K, the resonance due to the axial S-F's sharpened ($W_{½}$ = 220Hz), but the equatorial S-F resonance broadened to such an extent that it was barely visible as a shoulder on the side of the equatorial S-F resonance of [I] (estimated $W_{½}$ = 780Hz).

On further warming to 260K, the axial S-F resonance broadened further ($W_{½}$ = 450Hz) and the equatorial S-F resonance was no longer observed, implying that the fluxional process now involved all three S-F nuclei.

On recooling from this temperature to 195K, the individual resonances f_A, $f_{A'}$ and f_E were once again observed. However, if the solution was warmed above 260K and subsequently recooled then the ^{19}F resonances of [II] were no longer observed. Thus, we can conclude that [II] is thermally less stable than [I] as it decomposes at ~265K compared with 290K for the decomposition of [I].

Considering the difficulties outlined previously, it is not surprising that observation of the

v.t. ^{31}P n.m.r. spectra of [II] was not very fruitful. The only change which we could observe was that the apparent doublet at δ31.4 became a broad, featureless lump at 255K.

We have observed that the related complexes [I] and [II] behave differently in two respects;

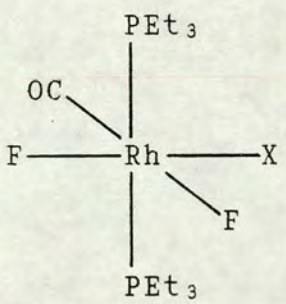
i) [I] is less fluxional than [II] and

ii) [I] is thermally more stable than [II].

In the ^{19}F n.m.r. spectrum, in contrast to the behaviour of the analogous Ir system, several other resonances were observed in the region associated with fluorine bonded to a Rh(III) centre[52].

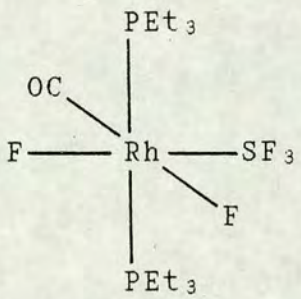
The most intense were two resonances, (A) and (B) which were both of the same intensity, aproximately 12% of the intensity of the Rh-F resonance of [I]. They were both doublets of doublets of triplets, (A) at δ-337.9 and (B) at δ-380.9 ($^2J_{F-F}$ = 123Hz). From the chemical shifts and the magnitudes of the coupling constants we can say that this complex must contain 6-coordinate Rh(III) with two phosphines and two inequivalent rhodium fluorides;

[figure 2.1.14]



[V]

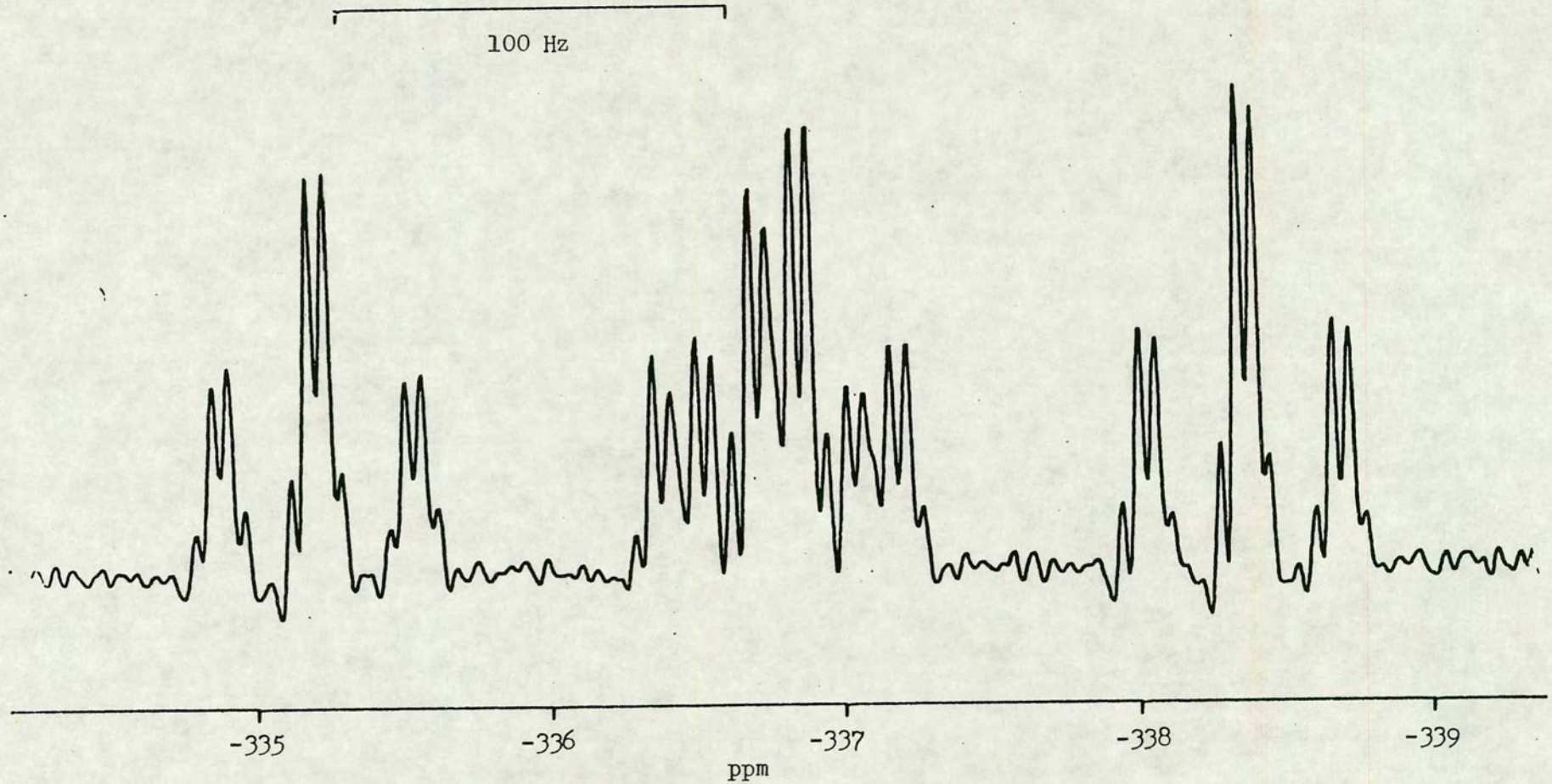
On warming to 235K the resonance at δ-337.9 became a sharp doublet of doublets of triplets of narrow quartets [figure 2.1.16]. Since we have only one coordination site left to assign and yet have a quartet still unaccounted for in the ^{19}F n.m.r. spectrum whose coupling is of the correct order of magnitude for a $^{3}J_{F-F}$ coupling, we can only presume that we have another $-SF_3$ group, implying that we have formed the complex; [figure 2.1.15]



[VI]

In the S-F region of the $^{19}F-\{^{1}H\}$ n.m.r. spectrum only one resonance of the correct intensity for this complex was observed. This was in the equatorial region, a triplet at δ-72.0 ($^{2}J_{F-F}$ = 69Hz) but we could not resolve it better to observe smaller couplings . In the axial S-F region of the spectrum there were no resonances which we could attribute to two axial S-F's, however, in subsequent work on the reaction of $Rh(CO)I(PEt_3)_2$ with SF_4 this complex was also present and in that case the axial S-F resonances were observed at δ75.6 and δ51.6. As these chemical shifts are very close to those observed for the much more intense axial S-F resonances of species [I] it is not surprising that

Figure 2.1.16 Expansion of A



they could not be detected in this reaction. This species was also detected in the reaction of $Rh(CO)Br(PEt_3)_2$ and $Rh(CO)NCS(PEt_3)_2$ with SF_4. In both reactions the axial resonances were also obscured by the axial S-F resonances of the major species, but in the thiocyanate reaction the proportion of this complex was high enough to extract more coupling constants from the equatorial S-F resonance. On warming to 245K the doublet of doublets of triplets of quartets lost its finer couplings and become a doublet of doublets of triplets. On recooling to 195K from 245K all three resonances reappeared in their original form showing the fluxional process to be reversible. No further changes were observed in the ^{19}F n.m.r. spectra until above 290K when the complex decomposed.

In the 145.085MHz $^{31}P-\{^1H\}$ n.m.r. spectrum of this reaction at 195K the only resonances visible of approximately the correct intensity to belong to complex [VI] were two broad lumps centred at 636.5. In the 81.015MHz $^{31}P-\{^1H\}$ n.m.r. spectrum these had resolved into two broad doublets. The separation of these doublets was ~220Hz which was similar to the separation of the b and c multiplets of the ABQRSTX pattern of [I], 227Hz. It is possible that these two multiplets are the two centre parts of an AB type pattern due to complex [VI]. If this is so then we must assume that the two outer parts are too weak to be distinguished from the baseline.

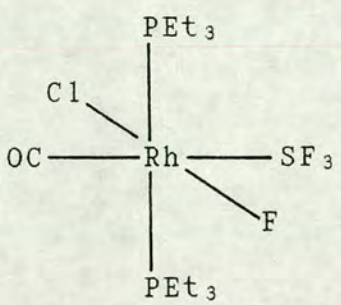
The doublet coupling observed was ~74Hz which is consistent with $^1J_{P-Rh}$ in a 6 coordinate complex. On warming to 210K the doublets began to broaden and on further warming to 215K both had coalesced to a single broad resonance. At 230K this resonance had now resolved to a broad doublet ($^1J_{P-Rh}$ = 76Hz) and remained thus up to 290K when the product decomposed.

Although our assignment appears to be based merely upon the couplings observed in two Rh-F resonances and single couplings in three S-F resonances, it is supported by the behaviour of the product of reaction of SF_4 with $Ir(CO)Cl(PEt_3)_2$[43]. This complex was studied to higher temperatures than we were able to reach in this system as it is not as thermally unstable as our $Rh-SF_3$ complexes. When the solution of $Ir(CO)ClF(PEt_3)_2SF_3$ was heated to the temperature at which its axial S-F's had become equivalent, the $^{19}F-\{^1H\}$ n.m.r. spectrum showed all three S-F's coupling equally to the Ir-F. Both of these observations, if applied to our spectrum, agree with our assignment of complex [VI], since at low temperature we saw the Rh-F coupling to three S-F's but did not see the axial S-F resonance and at higher temperature the Rh-F resonance lost its couplings to the S-F's. A very convincing piece of evidence for our assignment is the fact that these same ^{19}F resonances are seen in reactions of different halogenated starting materials .

In an attempt to provide further evidence for our assignment of this product a double resonance

experiment was performed [45]. On irradiation of the resonance at δ-380.9 in the ^{19}F n.m.r. spectrum, changes were observed only in the resonance observed at δ-337.9 which proved that these two resonances were indeed coupled to each other.

Also observed in the Rh(III)-F region of the $^{19}F-\{^{1}H\}$ n.m.r.spectrum was a low intensity doublet of triplets at δ-402.7 at approximately 5% of the intensity of each resonance of [I]. This resonance, being almost 50 p.p.m. to lower frequency than the Rh-F resonance of [I], was assigned as arising from F *trans* to halide rather than CO[52]. The only possible *trans* ligands were Cl or F; the chemical shift was not low enough for F *trans* to F, so it was assigned as F *trans* to Cl. This resonance integrated 1:1 with a triplet at δ-66.1 p.p.m. which lay close to that of the equatorial S-F resonance of [I]; a reexamination of the region associated with the axial S-F resonances revealed a broad resonance at δ61.7 which integrated to approximately twice the intensity of each of the resonances at δ-66.1 and δ-402.7. From these data we concluded that complex [VII], an isomer of [I] had been formed with SF_3 *trans* to CO; [figure 2.1.17]



[VII]

Since the axial S-F resonances have coalesced at a temperature as low as 195K, this product must already be undergoing fluxional behaviour that is fast on the n.m.r. timescale.

The broad resonance did not resolve into two resonances even on cooling to 170K, implying that the SF_3 group was considerably more fluxional in this complex than in [I]. ^{31}P n.m.r. spectroscopy was not useful in elucidating any more information about this complex as we merely observed broad, unresolved resonances in the expected region at the expected intensity.

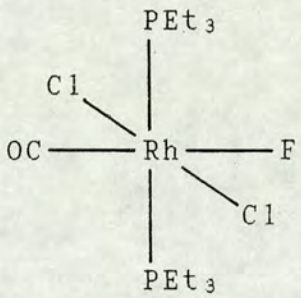
On warming to 215K, the triplet at δ-66.1 was no longer observed although the doublet of triplets at δ-402.7 remained. This implied that all three fluorines on sulphur had become equivalent, perhaps undergoing Berry-pseudorotation. On further warming, the resonance at δ-402.7 (the only ^{19}F resonance remaining visible from [VII]) decreased significantly in intensity and on recooling from 270K the residual resonances at δ-66.1 and δ-402.7 were so weak that it was almost impossible to observe them. Thus we can conclude that [VII] is thermally much less stable than its isomer [I]. As this complex was formed in such small amounts to begin with, it was not possible to say what the decomposition products were.

Several decomposition products were observed in the $^{19}F-\{^{1}H\}$ n.m.r. spectrum on recooling to 195K from

295K. The most prominent were;

i) the mono-fluoride complex [VIII] [52];

[figure 2.1.18]



[VIII]

observed as a doublet of triplets at δ-342.2 ($^{1}J_{F-Rh}$ = 105Hz and $^{2}J_{F-P}$ = 23Hz, $^{2}J_{F-C}$ = 65Hz from the reaction of SF_4 with $Rh(^{13}CO)Cl(PEt_3)_2$). The corresponding doublet of doublets was observed in the $^{31}P-\{^{1}H\}$ n.m.r. spectrum at δ28.3 ($^{1}J_{P-Rh}$ = 73Hz).

ii) Et_3PF_2; the product of oxidative fluorination of triethylphosphine [52]. This was observed as a wide doublet at δ-41.6 ($^{1}J_{P-F}$ = 556Hz). The corresponding triplet was observed in the $^{31}P-\{^{1}H\}$ n.m.r. spectrum at δ-9.2, and

iii) CD_2ClF, the product of fluorination of solvent [53]. This was observed as a quartet of 1:2:2:1 intensity at δ-174 ($^{1}J_{F-D}$ = 86Hz), indicating coupling to two identical nuclei of spin 1. Although the coupling seems rather large for a 2-bond F-D coupling constant, all the other data is consistent with our assignment of this resonance to CD_2ClF.

Since the monofluoride complex [VIII], formally the product of ClF addition to the starting material,

was observed in a 1:1 ratio with the CD_2ClF we assume that both were formed as part of the same decomposition process.

An attempt was made to obtain infra-red spectra of these complexes. However, due to the instability of these complexes to temperature, moisture and air, we were unable to obtain solution infra-red spectra with the equipment available. On pumping away solvent, in an attempt to obtain solid samples, we observed that SF_4 was also pumped away, indicating that reductive elimination of SF_4 was occurring.

Chapter Three.

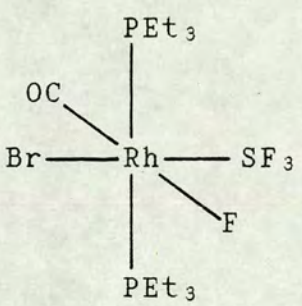
3.1 Reaction of $Rh(CO)Br(PEt_3)_2$ and SF_4.

As previously, the reaction was studied by $^{19}F-\{^1H\}$ n.m.r. spectroscopy at 195K [figure 3.1.2].

On melting, the solution became claret coloured as in the analogous chloride reaction and four resonances F_{1A}, $F_{1A'}$, F_{1E} and F_{1M} were observed with approximately equal intensities . These resonances each had the same multiplicity as the corresponding resonance observed in the analogous reaction with the chloride, 2.1, and were observed at δ75.8, δ44.0, δ-74.1 and δ-364.7. Parameters are detailed in tables 3.1.1 and 3.1.2.

As the chemical shifts of these four resonances were at slightly lower frequency than those of the products of the analogous reaction with the chloride and the resonances were almost identical in form, we can assign this spectrum as being due to complex [IX] which is similar but not identical to [I];

[figure 3.1.1]



[IX]

Figure 3.1.2; $^{19}F-\{^{1}H\}$ n.m.r. Spectrum of $Rh(CO)Br(PEt_3)_2 + SF_4$ at 195K

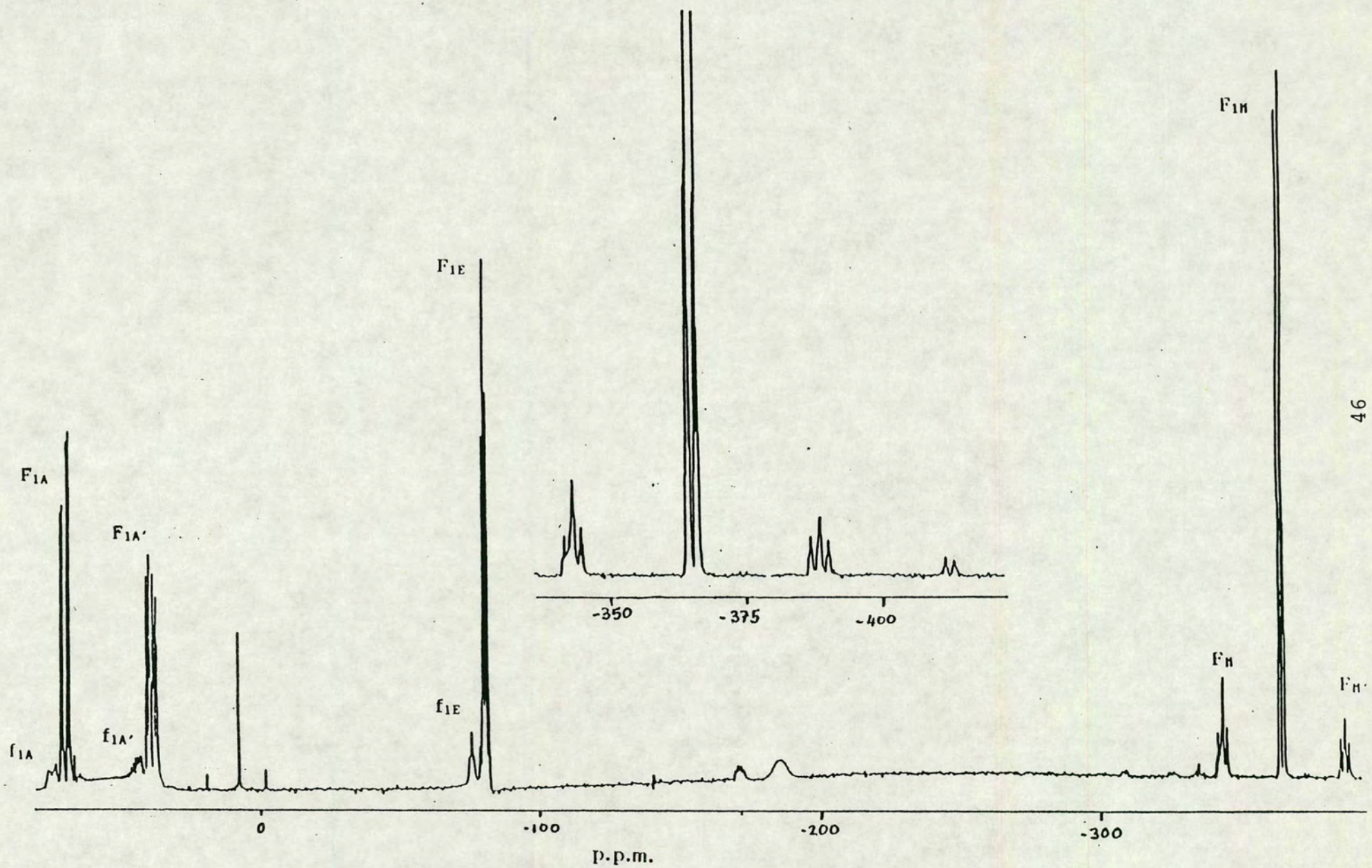


Table 3.1.1.

Chemical Shifts for Species [IX]/p.p.m.

S-F			Rh-F	P	
F_{1A}	$F_{1A'}$	F_{1E}	F_{1M}	P_A	P_B
75.8	44.0	-74.1	-364.7	30.9	24.9

Table 3.1.2.

Coupling Constants for Species [IX]/Hz

Nuc.	F_{1A}	$F_{1A'}$	F_{1E}	F_{1M}	P_A	P_B	Rh
F_{1A}	-	185	60	n.o.	n.o.	4	10
$F_{1A'}$	185	-	76	10	26	n.o.	16
F_{1E}	60	76	-	n.o.	7	7	15
F_{1M}	n.o.	10	n.o.	-	28	28	114
P_A	n.o.	26	7	28	-	416	75
P_B	4	n.o.	8	26	416	-	75

The $^{31}P-\{^1H\}$ n.m.r. spectrum at 195K also supported this conclusion, showing an ABQRSTX pattern [figure 3.1.3].

Calculating the positions of the A and B parts as previously gave;

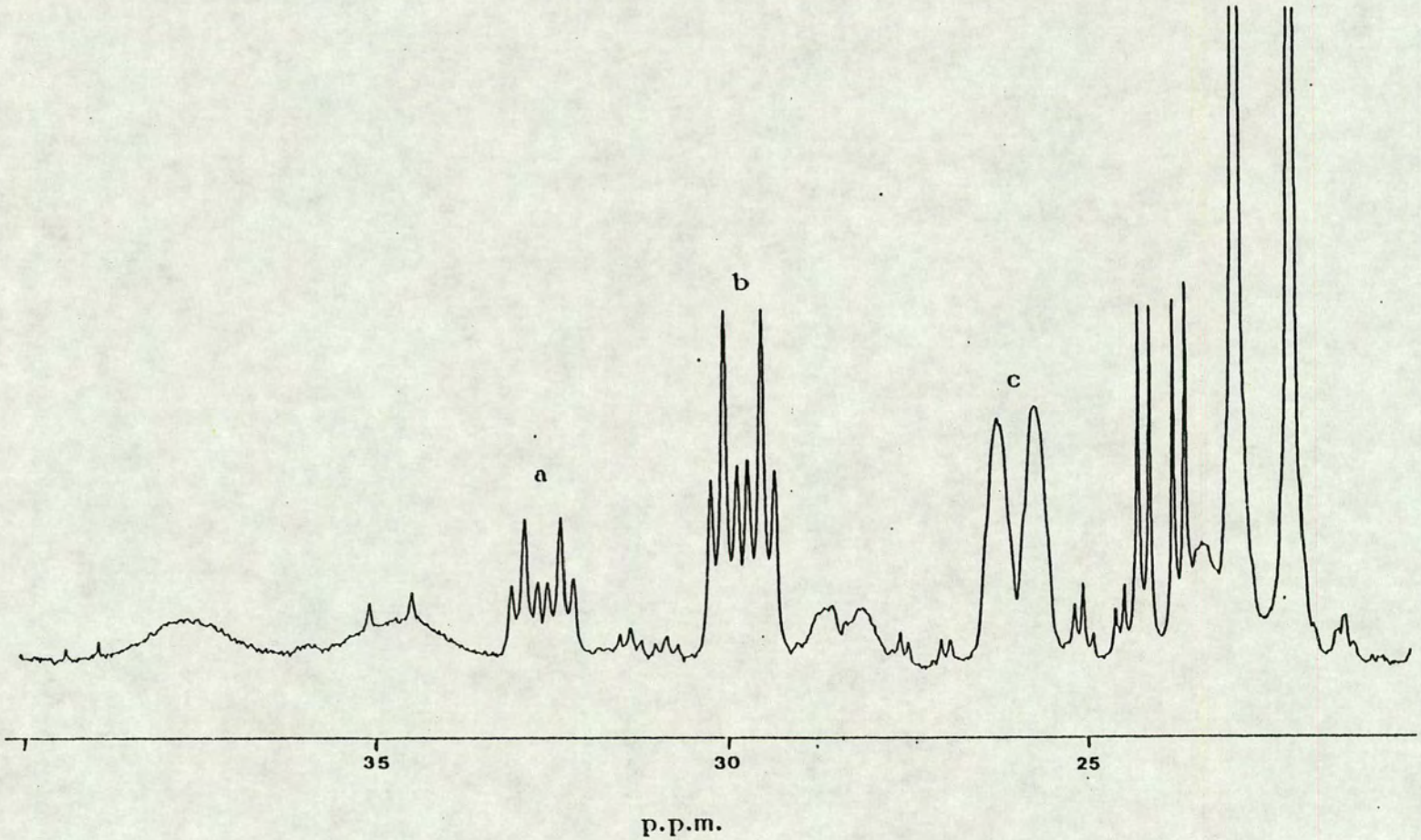
$$P_A = 630.9 \text{ and } P_B = 624.9.$$

On warming, the $^{19}F-\{^1H\}$ n.m.r. spectrum was observed to change. At 260K the two axial S-F resonances and the Rh-F resonance began to broaden but the equatorial S-F resonance remained sharp as in the analogous chloride system.

At 265K only the mutual couplings could be observed in the axial S-F resonances and the equatorial

Figure 3.1.3; $^{31}P-\{^{1}H\}$ n.m.r. Spectrum of $Rh(CO)Br(PEt_3)_2 + SF_4$ at 195K

145.785MHz



S-F peak had lost all of its couplings.

At 280K all three S-F resonances had lost all couplings and the Rh-F resonance had resharpened to a doublet of triplets, losing the $^{3}J_{F-F}$ coupling to the second highest S-F.

On further warming to 295K the axial S-F resonances had almost coalesced but decomposition occurred at this temperature so that, as in the analogous chloride system, we could not study the fluxionality past the stage at which the two axial S-F's became equivalent.

The $^{31}P-\{^{1}H\}$ n.m.r. spectrum on warming showed similar effects to those of the chloride system. Around 255K both the A and B parts of the spectrum began to lose their fine structure, showing only doublets in each part and at 275K only a very broad resonance was observed which could not be resolved. This did not change on further warming and at 295K it had disappeared. On recooling to 195K the AB type pattern did not reappear, indicating that decomposition had occurred.

On comparing the n.m.r. spectra of the products of the reactions of SF_4 with $Rh(CO)Cl(PEt_3)_2$ and $Rh(CO)Br(PEt_3)_2$ at different temperatures we can see that the bromide complex [IX] is less fluxional than the chloride complex [I]. We shall discuss this result later in this chapter.

As previously, we also observed resonances due

to other fluorine containing compounds.

Three resonances f_{1A}, $f_{1A'}$ and f_{1E} of approximately equal intensity at around 10% the intensities of F_{1A}, $F_{1A'}$ and F_{1E} were observed at slightly higher frequencies than the three S-F resonances of [IX] [figure 3.1.2]. These were a doublet of doublets of doublets of doublets at δ82.0, a doublet of doublets of doublets of doublets at δ54.2 and a doublet of doublets of doublets of triplets at δ-68.3. Parameters are detailed in tables 3.1.3 and 3.1.4.

Table 3.1.3.

Chemical Shifts for Species [X]/p.p.m.

S-F			P
f_A	$f_{A'}$	f_E	P
82.0	54.2	-68.3	28.0

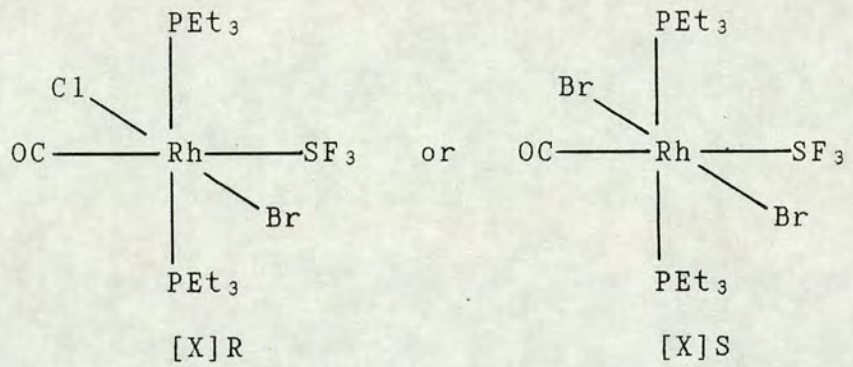
Table 3.1.4.

Coupling Constants for Species [X]/Hz

Nuc.	f_A	$f_{A'}$	f_E	P	Rh
f_A	-	184	54	12	12
$f_{A'}$	184	-	73	16	16
f_E	54	73	-	15	15
P	12	16	15	-	74
Rh	12	16	15	74	-

There was no fluorine resonance observed in the region associated with fluorine bonded to Rh(III)[47] at the correct intensity, so on this basis and by analogy with reaction 2.1 we have assigned these resonances as being due to the SF_3 group of a complex [X];

[figure 3.1.4]



[X]R [X]S

Since neither chloride nor bromide has a nuclear spin of ½ we could not use n.m.r. spectroscopy to distinguish between these two possible products.

If [X] were complex [X]S, the second bromide must have come from another molecule of $Rh(CO)Br(PEt_3)_2$ and thus the $^{31}P-\{^1H\}$ n.m.r. spectrum should have shown resonances due to a Rh complex without bromide. There are no obvious resonances showing this, but it would be very difficult to pick out such resonances from this complicated spectrum.

If [X] were complex [X]R, then the chloride must have come from interaction with solvent. We have already seen, in the previous chapter, that reaction of CD_2Cl_2 is possible and thus the $^{19}F-\{^1H\}$ n.m.r. spectrum was reobserved for signs of this; at δ-174 a 1:2:2:1 quartet was observed due to CD_2ClF. Although we have no firm evidence that [X] is either [X]R or [X]S we feel that it is most likely that [X]R is the product since in all the previous work involving oxidative addition reactions of inorganic fluorides to rhodium complexes [41-43,47,52] we have never observed halide substitution

between two rhodium molecules but we have, on several occasions, observed fluorination of solvent.

As with reaction 2.1 it was difficult to assign the $^{31}P-\{^{1}H\}$ n.m.r. resonance of this complex. At 145.785Mz we observed a broad doublet at δ28.0 ($^{1}J_{P-Rh}$ = 74Hz). By comparison with the ABQRSTX pattern of [IX], the intensity of this resonance was approximately that expected for [X] but we cannot be certain. We could not observe this resonance in the 81.015MHz n.m.r. spectrum as it was obscured by the b and c multiplets of the ABXQRST pattern of [IX].

On warming, the $^{19}F-\{^{1}H\}$ n.m.r. spectrum changed, again indicating fluxional behaviour.

At 220K the axial S-F resonances of [X] had broadened, showing only their mutual couplings, and the equatorial S-F resonance remained unchanged. On warming to 225K, however, the two axial S-F resonances were barely distinguishable from the baseline and the equatorial S-F resonance had now broadened so much that it had lost all of its couplings. On further warming to 235K the equatorial S-F resonance disappeared completely and there was no evidence of the axial S-F resonances either. Indeed, on recooling to 195K none of the three S-F resonances of [X] was observed, indicating that decomposition had occurred.

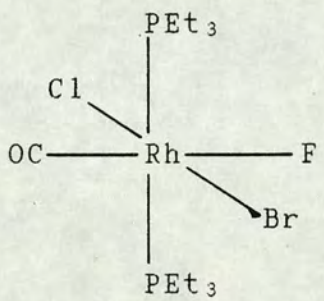
Two major new resonances in the $^{19}F-\{^{1}H\}$ n.m.r. spectrum were observed after recooling from 235K;

a) a doublet at δ-41.6 due to Et_3PF_2 appeared

and

b) a doublet of triplets at δ-355.4 which we have assigned as the previously reported complex [XI] [52];

[figure 3.1.5]



[XI]

($^{1}J_{F-Rh}$ = 105Hz, $^{2}J_{F-P}$ = 25Hz).

The corresponding doublet of doublets was observed in the $^{31}P-\{^{1}H\}$ n.m.r. spectrum at δ23.3 ($^{1}J_{P-Rh}$= 73Hz).

If complex [XI] is, indeed, a decomposition product of [X] then this is yet further evidence for our assignment of [X] having a Cl and Br rather than two Br ligands.

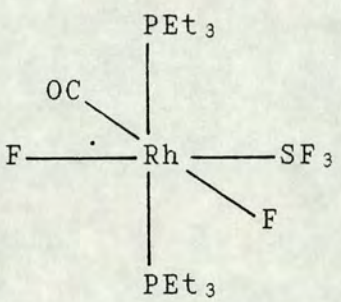
These results indicate that complex [X] is less thermally stable than [IX], decomposing to give Et_3PF_2 and $Rh(CO)ClBrF(PEt_3)_2$.

The fluxional process which [X] undergoes appears to be similar to that of all the previously discussed Rh-SF_3 complexes. However, although complex [IX] is less fluxional than its chloride analogue [I], [X] appears to be significantly more fluxional than the

analogous chloride complex [II].

Other significant features of the $^{19}F-\{^{1}H\}$ n.m.r. spectrum at 195K were two doublets of doublets of triplets, F_M and $F_{M'}$, at δ-337.7 and δ-381.1 in the ratio 1:1 at approximately 7% of the intensity of the resonances of [IX]. These resonances lay at the same chemical shifts and had the same multiplicities and coupling constants as the two Rh-F resonances assigned to complex [VI];

[figure 3.1.6]



[VI]

We therefore observed the S-F region of the spectrum and, indeed, found the corresponding triplet-like equatorial S-F resonance at δ-72.1 and, as in the previous reaction, there were no obvious axial S-F resonances.

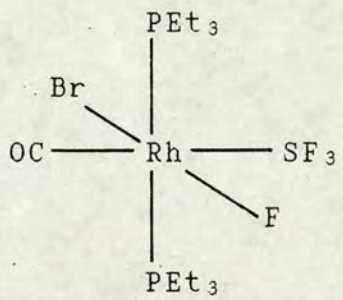
On warming, these resonances behaved in an identical manner to those of [VI] and thus we have assigned these three resonances as belonging to complex [VI].

The $^{31}P-\{^{1}H\}$ n.m.r. spectrum also showed the broad doublet at δ36.5 whose behaviour on warming was also identical to that of the resonance which we

assigned previously to complex [VI]. This confirms that our assignment of the ^{31}P resonance of this complex is correct.

The only other significant feature in the $^{19}F-\{^{1}H\}$ n.m.r. spectrum at 195K was a very weak doublet of apparent triplets at δ-410 ($^{1}J_{F-Rh}$ = 120Hz, $^{2}J_{F-P}$ ~25Hz). This integrated at approximately 1:1 with a triplet in the equatorial S-F region at δ-67.0. Both were at approximately 2% of the intensity of the F resonances of [IX]. Due to the weakness of these two resonances it was not possible to gain accurate chemical shifts and coupling constants, but by analogy with reaction 2.1 we believe that these resonances must be due to the complex;

[figure 3.1.7]



[XII]

On warming to 210K the equatorial S-F resonance disappeared into the baseline and the Rh-F resonance became a broad doublet indicating possible fluxional behaviour. On further warming to 240K the Rh-F resonance disappeared and on recooling to 195K neither resonance reappeared indicating decomposition.

We can thus conclude that $Rh(CO)Br(PEt_3)_2$

reacts with SF_4 in a similar manner to its chloride analogue. However, the complexes thus formed are less fluxional than the analogous chloride complexes although both complexes have similar thermal stability.

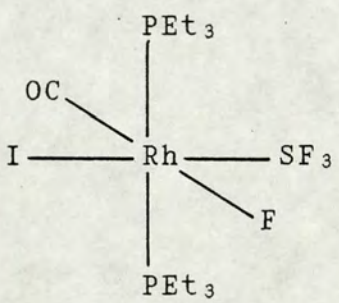
3.2 Reaction of $Rh(CO)I(PEt_3)_2$ and SF_4.

This reaction was carried out as previously and observed by ^{19}F n.m.r. spectroscopy.

On melting, the solution again became claret coloured and four resonances were detected, F_{2A}, $F_{2A'}$, F_{2E} and F_{2M} at equal intensities [figure 3.2.2]. These four resonances had the same multiplicities as those resonances observed in the analogous chloride and bromide reactions. These lay at δ72.4, δ39.9, δ-77.3 and δ-377.0. Parameters are detailed in tables 3.2.1 and 3.2.2.

These chemical shifts are slightly lower than those of the analogous chloride and bromide complexes and, thus we have assigned them as arising from complex [XIII];

[figure 3.2.1]



[XIII]

Table 3.2.1.

Chemical Shifts for Species [IX]/p.p.m.

S-F		Rh-F		P	
F_{2A}	$F_{2A'}$	F_{2E}	F_{2M}	P_A	P_B
72.4	39.9	-77.3	-377.0	27.4	21.8

Figure 3.2.2; $^{19}F - \{^{1}H\}$ n.m.r. spectrum of $Rh(CO)I(PEt_3)_2 + SF_4$ at 195 K

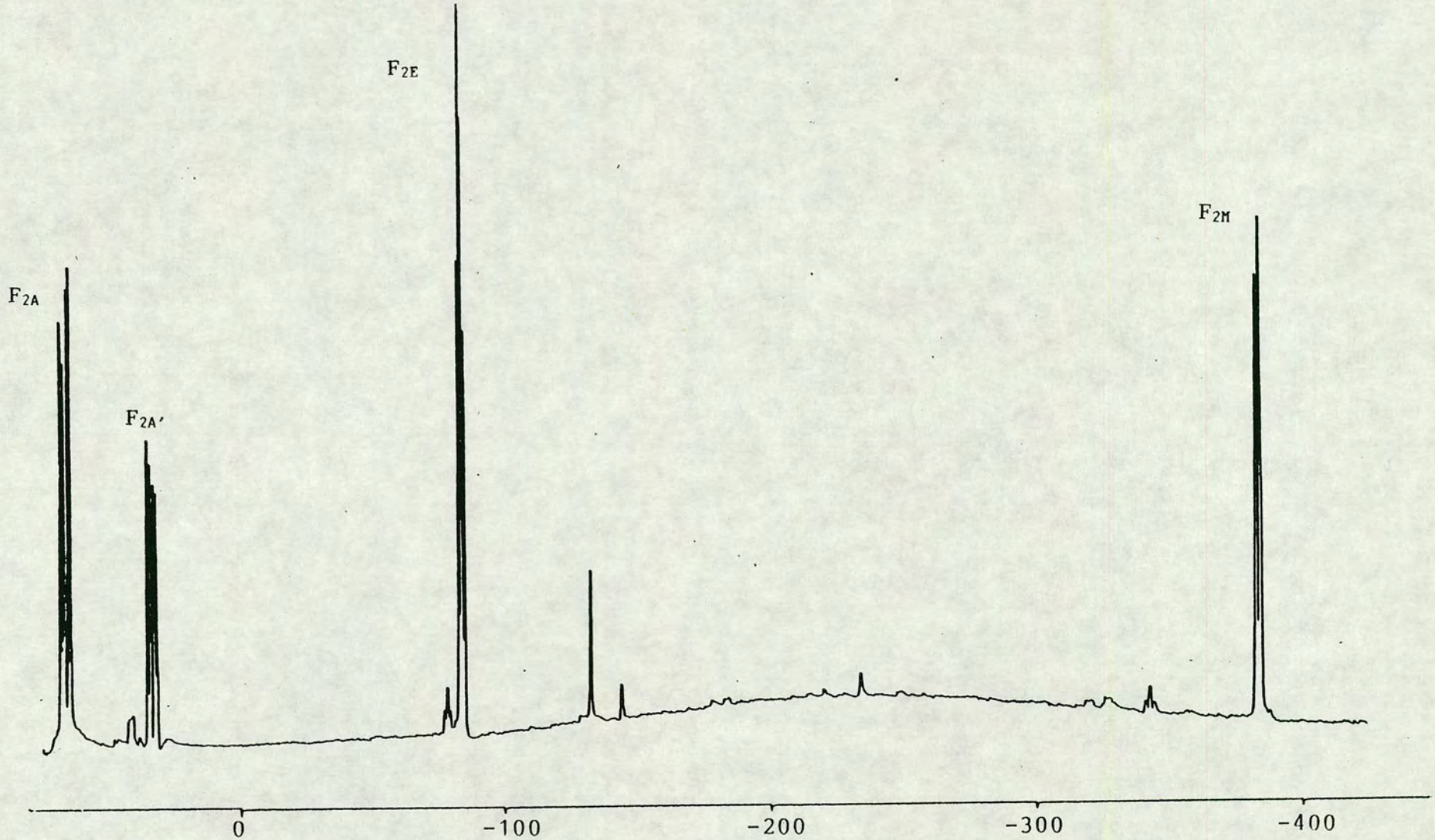


Table 3.2.2.

Coupling Constants for Species [IX]/Hz.

Nuc.	F_{2A}	$F_{2A'}$	F_{2E}	F_{2M}	P_A	P_B	Rh
F_{2A}	-	187	67	n.o.	n.o.	4	11
$F_{2A'}$	187	-	83	10	28	n.o.	16
F_{2E}	67	83	-	n.o.	8	8	15
F_{2M}	n.o.	10	n.o.	-	28	28	114
P_A	n.o.	28	8	28	-	416	75
P_B	4	n.o.	8	28	416	-	75

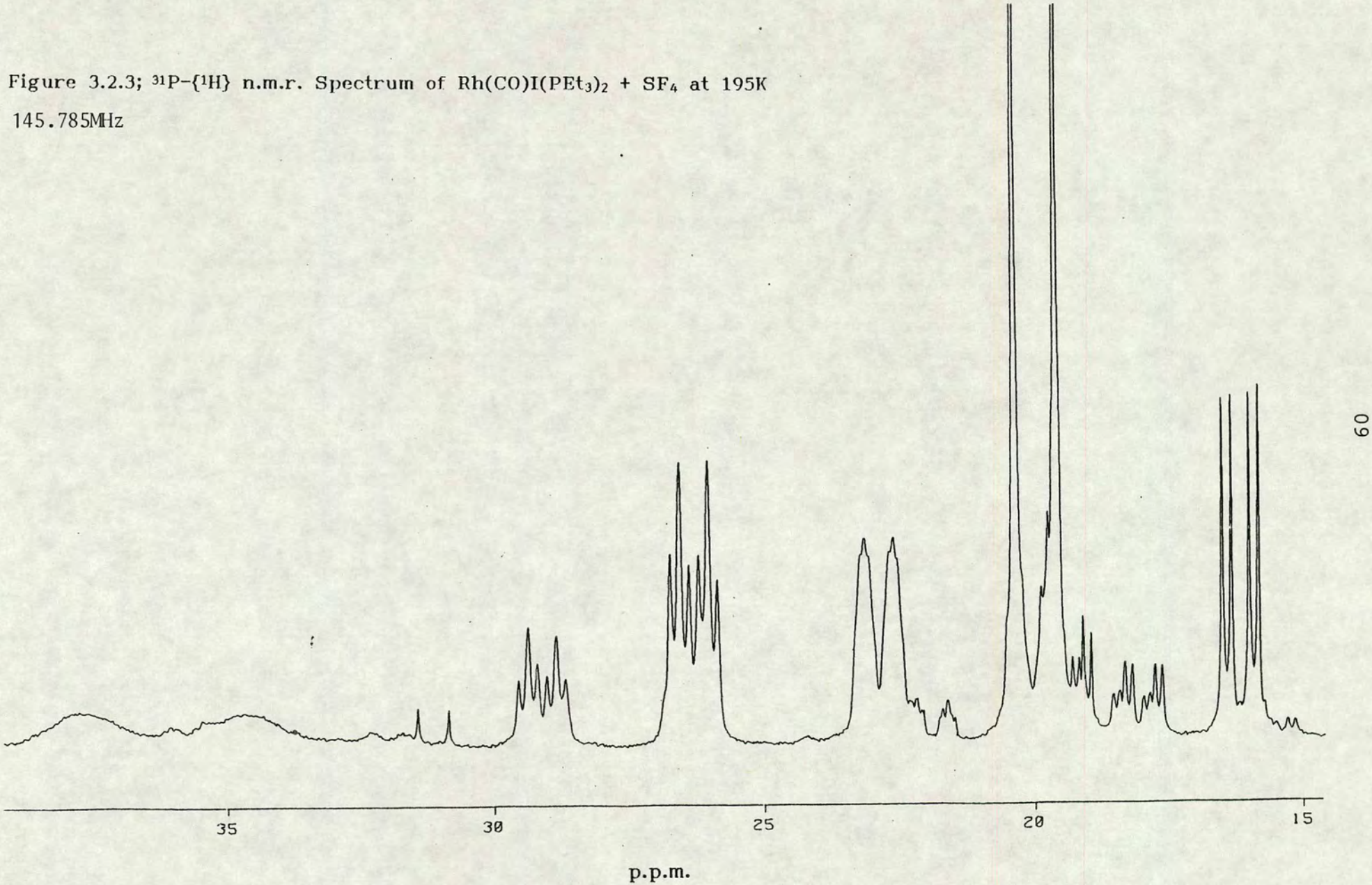
The $^{31}P-\{^1H\}$ n.m.r. spectrum was consistent with this assignment, showing an ABQRSTX pattern with P_A at δ27.4 and P_B at δ21.8 [figure 3.2.3].

On warming, the $^{19}F-\{^1H\}$ n.m.r. spectrum did not change until a rather high temperature was reached. At 275K the axial S-F resonances began to broaden and only showed their couplings to each of the other S-F's. At 280K only the mutual couplings could be observed in the two axial S-F resonances and the equatorial S-F resonance had lost all of its couplings. At 290K all three S-F resonances had lost all couplings and had begun to broaden ($W_{½AX}$= 400Hz). The Rh-F resonance had sharpened to a doublet of triplets at this temperature, losing its coupling to F_{2A}. Above this temperature decomposition was observed to occur.

The $^{31}P-\{^1H\}$ n.m.r. spectra were not very informative on warming. At 270K both the A and B parts began to lose their fine couplings. At 280K only a very broad resonance was observed, from which no couplings

Figure 3.2.3; $^{31}P-\{^{1}H\}$ n.m.r. Spectrum of $Rh(CO)I(PEt_3)_2$ + SF_4 at 195K

145.785MHz



could be resolved. This resonance did not change further until decomposition occurred around 295K.

By comparison with the analogous chloride and bromide complexes, [I] and [IX], we can see that there is a trend in the fluxionality of the SF_3 group in these complexes as we vary the halide in the starting material.

In an attempt to better understand the reasons for this variation we decided to extend the series of complexes studied by reacting pseudohalide complexes with SF_4. These results will be studied in the following section, 3.3.

The $^{19}F-\{^1H\}$ n.m.r. spectrum at 195K was much simpler in this reaction than in either of the previous two discussed in this thesis. The only other resonances observed were;

i) those previously assigned as $Rh(CO)F_2(PEt_3)_2SF_3$, [VI],

ii) that due to CD_2ClF and

iii) that due to Et_3PF_2.

We could, however, observe the axial S-F resonances of $Rh(CO)F_2(PEt_3)_2SF_3$. These were observed at δ75.6 and δ51.6. From their chemical shifts these resonances would have been obscured by the axial S-F resonances of all the major species in the analogous chloride and bromide. They were very broad, only showing their mutual coupling which is consistent with our

previous assignment of this complex as being fluxional even at 195K.

We were unable to extract all the couplings from these resonances but we have been able to obtain more information on this complex than we were able to previously. Parameters are detailed in tables 3.2.3 and 3.2.4.

Table 3.2.3.

Chemical Shifts for Species [VI]/p.p.m.

S-F			Rh-F		P
F_A	$F_{A'}$	F_E	F_M	$F_{M'}$	P_A
75.6	51.6	-72.1	-337.7	-381.1	36.5

Table 3.2.4.

Coupling Constants for Species [VI]/Hz

Nuc.	F_A	$F_{A'}$	F_E	F_M	$F_{M'}$	P_A	Rh
F_A	-	n.o.	69	5	n.o.	n.o.	n.o.
$F_{A'}$	n.o.	-	n.o.	5	n.o.	n.o.	n.o.
F_E	n.o.	n.o.	-	5	n.o.	n.o.	n.o.
F_M	5	5	5	-	123	23	112
P_A	n.o.	n.o.	n.o.	23	23	-	76

Another result of having fewer products was that we could now observe the ^{31}P resonance for this complex without the problem of superposition of other resonances on it.

At 195K the $^{31}P-\{^1H\}$ n.m.r.spectrum showed the two broad humps centred at δ36.5 which we previously assigned as being the two centre parts of an AB type

pattern.

We were now in a better position to study the fluxional behaviour of this complex by observing the $^{19}F-\{^{1}H\}$ n.m.r. spectrum on warming. Thus, at 200K the axial S-F resonances were observed to broaden, only keeping their mutual coupling, whilst the other three resonances remained unchanged. At 210K the axial S-F resonances had broadened further, losing their mutual coupling with no change in the other resonances being observed. At 235K the coalesced resonance of the axial S-F's was observed at δ65.4 at which temperature the equatorial S-F resonance had now begun to broaden. On further warming to 245K the equatorial S-F resonance no longer showed any couplings and both Rh-F resonances had lost their narrow quartet coupling, becoming doublets of doublets of triplets. No further change was observed on the spectrum until it reached 265K when all of the S-F resonances disappeared but the Rh-F resonances remained unchanged. At 290K all the resonances arising from complex [VI] had disappeared and on recooling to 195K none of them reappeared, indicating that decomposition had occurred. However, on recooling to 195K from 280K, the original spectrum was again observed.

As mentioned briefly before, we were also able to study the variable temperature $^{31}P-\{^{1}H\}$ n.m.r. spectra more fully in this system. At 195K the resonance assigned as arising from the PEt_3 groups of complex [VI] was observed as two broad lumps at δ36.5. On warming to

200K both parts had coalesced to a single broad, unresolved resonance. At 240K this resonance had become a sharp doublet of triplets ($^{1}J_{P-Rh}$= 80Hz and $^{2}J_{P-F}$ = 23Hz) and remained so until decomposition occurred at 290K. All of these observations are consistent with our previous assignment of the spectra belonging to this complex and indeed we have been able to gain further support for our assignment in this particular reaction by observing the axial S-F resonances.

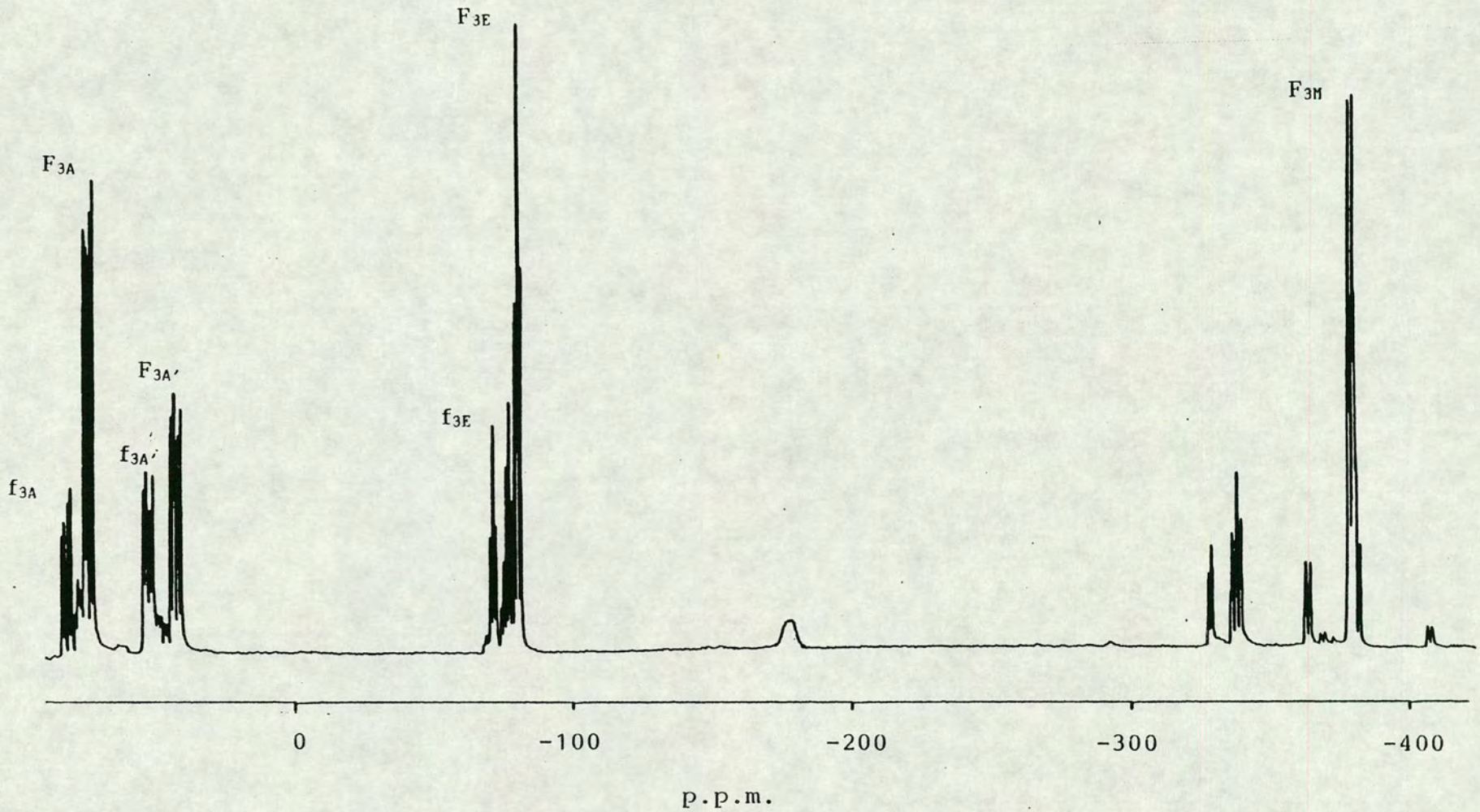
3.3 Reaction of $Rh(CO)NCS(PEt_3)_2$ with SF_4.

We have seen, in the reactions of SF_4 with the complexes $Rh(CO)X(PEt_3)_2$ [X = Cl, Br, I], that by varying the halide we affect the fluxional behaviour of the products formed. In an attempt to understand the reasons for these observations we decided to extend this series of complexes by using pseudohalide[54] starting materials.

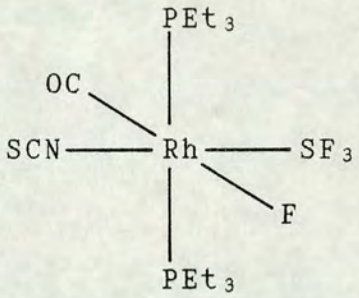
The reaction of SF_4 with $Rh(CO)NCS(PEt_3)_2$ was once again detected by $^{19}F-\{^1H\}$ n.m.r. spectroscopy at 195K. On melting, the solution became deep orange and a spectrum containing many resonances was observed [figure 3.3.1]. The most intense were four resonances F_{3A}, $F_{3A'}$, F_{3E} and F_{3M} at equal intensities. They were a doublet of doublets of doublets of doublets at δ73.7, a doublet ofdoublets of doublets of doublets of doublets at δ42.0, a doublet of doublets of doublets of triplets at δ-80.4 and a doublet of triplets of doublets at δ-377.9. Parameters are detailed in tables 3.3.1 and 3.3.2.

These resonances all had the same multiplicities as those of the major species observed in the analogous halide reactions and thus we have assigned these resonances as arising from complex [XIV];

Figure 3.3.1; $^{19}F - \{^{1}H\}$ n.m.r. spectrum of $Rh(CO)NCS(PEt_3)_2 + SF_4$ at 195 K



[figure 3.3.2]



[XIV]

Since all the SF_3 complexes studied are unstable to air it was not possible to obtain solution infrared spectra of these complexes and on pumping away solvent we observed reductive elimination of SF_4 as previously.

Generally, in rhodium complexes the thiocyanate is sulphur bound[55,56]. However, the infra-red spectrum of the starting material suggested that the NCS group was actually nitrogen-bound i.e. an isothiocyanate. In the nujol mull infra-red spectrum of $Rh(CO)NCS(PEt_3)_2$ we observed a strong band at ϕ = 2055cm^{-1}. This is the region expected for the C-N stretch in a nitrogen-bound NCS group, whereas the expected region for this vibration in a sulphur bound complex is 2080-2120cm^{-1} [57]. However, there are linkage isomers where this vibration is greater for the nitrogen-bonded isomer than for the sulphur bonded one[58,59]. We assume that the product has the same form as the starting material.

Table 3.3.1.

Chemical Shifts for Species [XIV]/p.p.m.

S-F			Rh-F	P	
F_{3A}	$F_{3A'}$	F_{3E}	F_{3M}	P_A	P_B
73.7	42.0	-80.4	-377.9	32.9	24.3

Table 3.3.2.

Coupling Constants for Species [XIV]/Hz

Nuc.	F_{3A}	$F_{3A'}$	F_{3E}	F_{3M}	P_A	P_B	Rh
F_{3A}	-	183	73	n.o.	n.o.	4	10
$F_{3A'}$	183	-	85	10	28	n.o.	17
F_{3E}	73	85	-	n.o.	7	7	14
F_{3M}	n.o.	10	n.o.	-	26	26	120
P_A	n.o.	28	7	26	-	411	74
P_B	4	n.o.	7	26	411	-	74

In order to determine absolutely which linkage isomer is present, single crystals of $Rh(CO)NCS(PEt_3)_2$ were grown and the x-ray crystal structure was solved[60].

This confirmed our observations from the infrared spectrum showing that the thiocyanate group was nitrogen-bonded to the rhodium [figure 3.3.3]. The space-filled diagram of this structure shows one likely reason why it is the isothiocyanate which forms [figure 3.3.4]. The steric bulk of sulphur is so large that it is difficult imagining it fitting inbetween the layers formed by the ethyl groups of the PEt_3 ligands.

The 81.015MHz $^{31}P-\{^1H\}$ n.m.r. spectrum showed several very complicated and asymmetric resonances in the region associated with PEt_3 groups bonded to a

Figure 3.3.3; X-ray Crystal Structure of Rh(CO)NCS(PEt3)2.

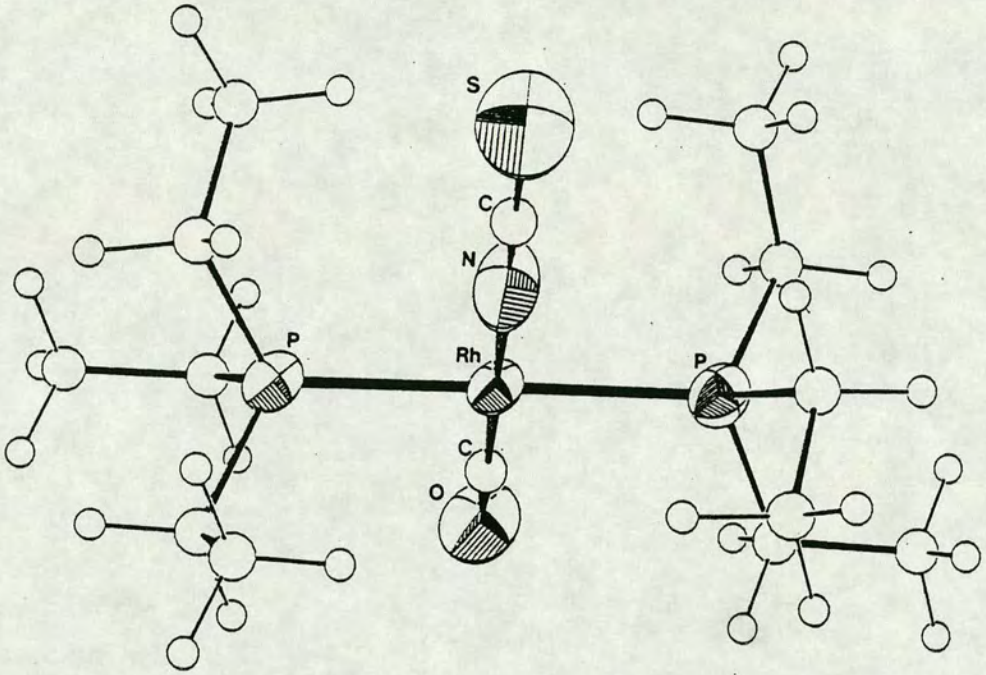
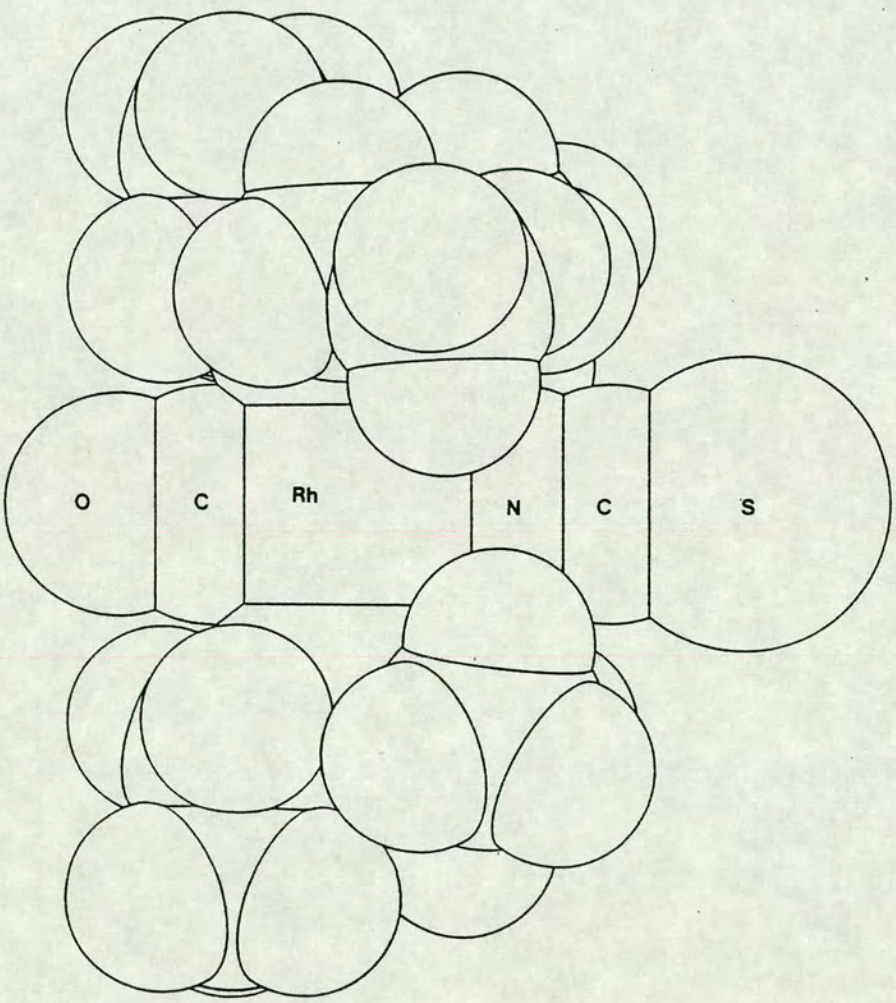


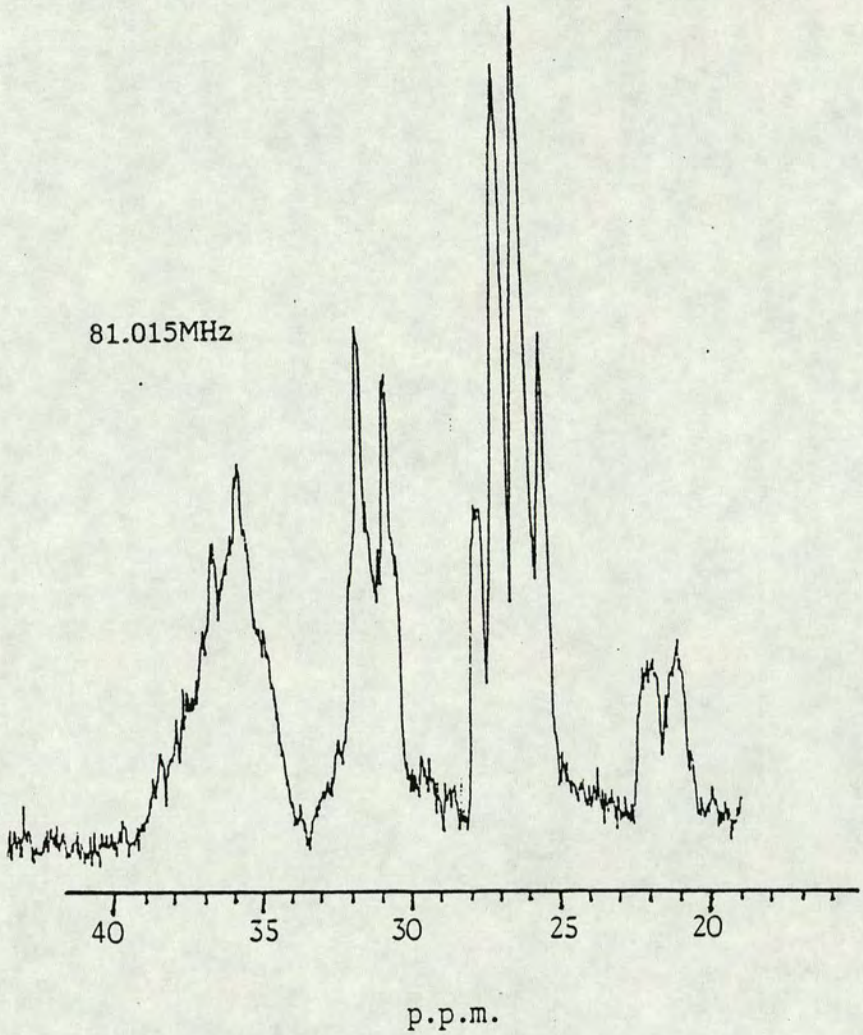
Figure 3.3.4; Space-filled Diagram of Rh(CO)NCS(PEt3)2.



Rh(III) centre[50]. However, on reobserving at 145.785MHz, the spectrum became rather simpler [figure 3.3.5]. We have assigned the major resonance, an ABQRSTX pattern as arising from the two inequivalent PEt_3 groups of complex [XVI]. As previously, calculations gave us the positions of both phosphine resonances as P_A = δ32.9 and P_B = δ24.3.

As in all previous Rh-SF_3 complexes studied on warming, the $^{19}F-\{H\}$ n.m.r. spectrum changed in a manner suggesting fluxional behaviour [figure 3.3.6]. At 260K the two axial S-F resonances began to lose their couplings, whilst the equatorial S-F and the Rh-F resonances remained sharp. At 265K only the mutual couplings could be observed in the two axial S-F resonances and also at this temperature the equatorial S-F resonance began to lose its couplings. On further warming to 270K the axial S-F resonances had broadened considerably ($W_{½AX}$ = 350Hz), losing all their couplings while the equatorial S-F resonance only showed its couplings to the axial S-F's and the Rh-F resonance had lost its coupling to the one axial S-F, becoming a doublet of triplets. At 280K the equatorial S-F resonance had lost all of its couplings and began to broaden and the axial S-F resonances had broadened much more ($W_{½AX}$ = 500Hz) but the Rh-F resonance remained a sharp doublet of triplets. At 290K all three S-F resonances had broadened much more ($W_{½AX}$ =900Hz), with only the Rh-F resonance remaining sharp. At 300K the

Figure 3.3.5; $^{31}P-\{^{1}H\}$ n.m.r. Spectrum of $Rh(CO)NCS(PEt_3)_2$ + SF_4 at 195K



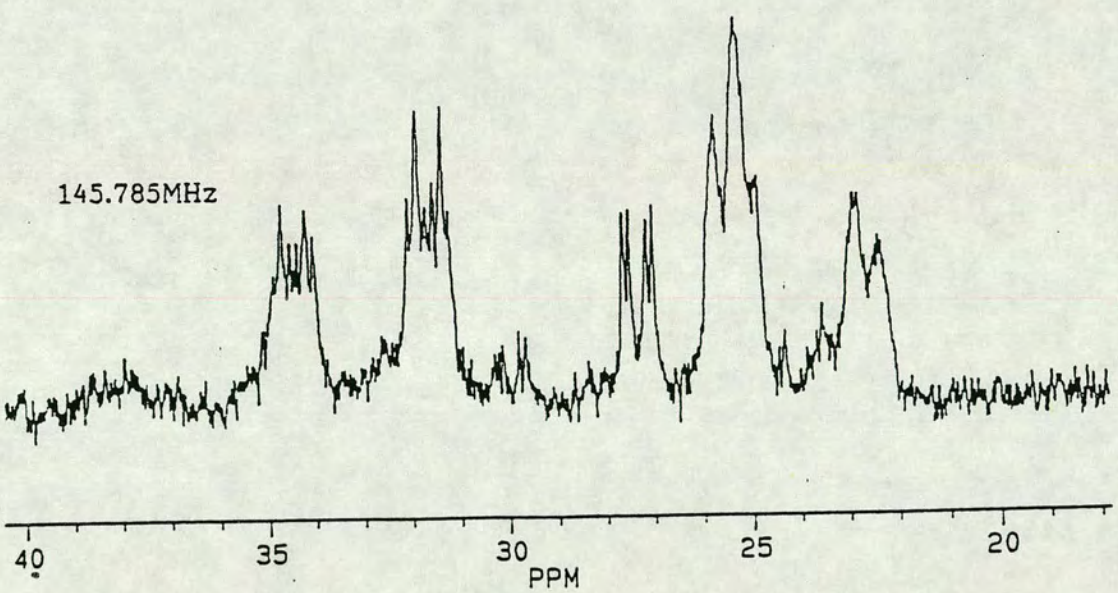
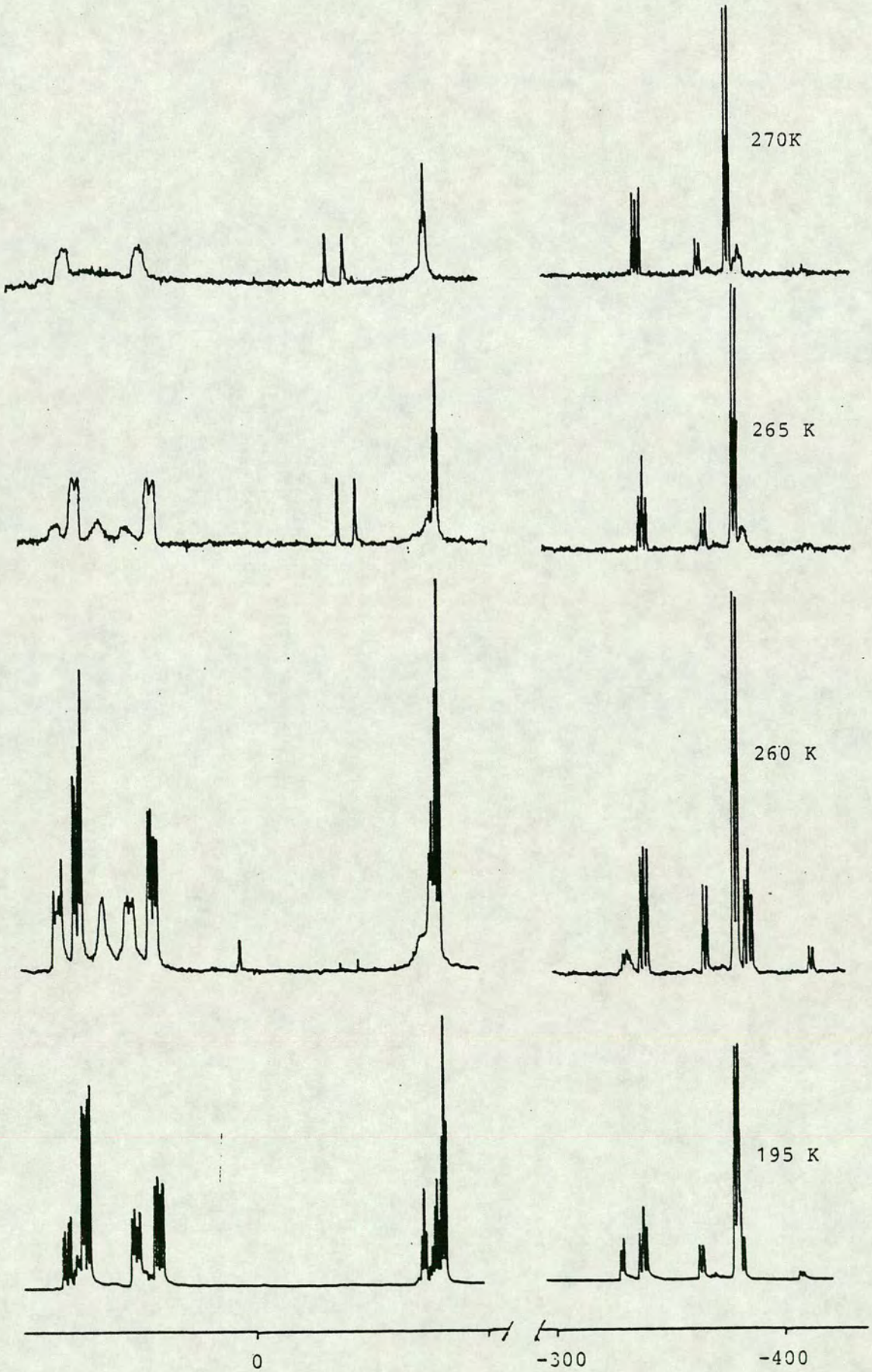


Figure 3.3.6; **V**.t. ^{19}F spectra of $Rh(CO)NCS(PEt_3)_2 + SF_4$



axial S-F resonances were so broad that they were almost indistinguishable from the baseline of the spectrum.

On warming above 300K the complex decomposed and as a result we observed characteristic ^{19}F resonances for HF as well as SiF_6^{2-} and BF_4^- [61] (the products of HF attack on glass), also Et_3PF_2 and several low abundance Rh-F resonances which were in the correct region for simple 6 coordinate Rh(III)-F complexes [47].

The $^{31}P-\{^1H\}$ n.m.r. spectra were consistent with the ^{19}F data, showing similar behaviour to that observed in the analogous halide reactions. At 260K both the A and B parts of the spectrum began to lose their couplings and at 300K a broad doublet appeared to be present ($^1J_{P-Rh}$ = 78Hz).

Also present in the $^{19}F-\{^1H\}$ n.m.r. spectrum of this system at 195K were several other resonances. The three most prominent of these f_{3A}, $f_{3A'}$ and f_{3E} were a doublet of doublets of doublets of doublets at δ81.9, a doublet of doublets of doublets of doublets at δ52.7 and a doublet of doublets of doublets of triplets at δ-77.7 respectively. Parameters are detailed in tables 3.3.3 and 3.3.4. These three resonances were in a 1:1:1 ratio and their intensities were at approximately 50% of the intensities of each resonance of [XIV].

By analogy with the previously discussed reactions we have assigned these resonances as arising from complex [XV], $Rh(CO)ClNCS(PEt_3)_2SF_3$.

Table 3.3.3.

Chemical shifts for species [XV]/p.p.m.

S-F		
f_{3A}	$f_{3A'}$	f_{3E}
82.0	51.9	-77.6

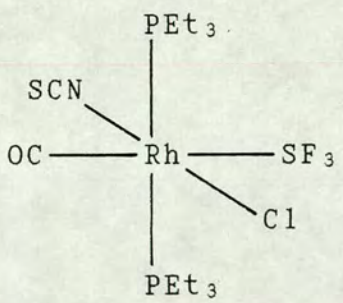
Table 3.3.4.

Coupling constants for Species [XV]/Hz

Nuc.	f_{3A}	$f_{3A'}$	f_{3E}	P_A	P_B	Rh
f_{3A}	-	180	64	n.o.	18	18
$f_{3A'}$	180	-	77	16	n.o.	16
f_{3E}	64	77	-	6	6	13

As in the reaction of SF_4 with $Rh(CO)Cl(PEt_3)_2$, a sample of ^{13}C enriched starting material was prepared and reacted with SF_4. Once again, only two extra couplings were observed in the $^{19}F-\{^1H\}$ n.m.r. spectrum. The first was the 2-bond C-F coupling in the Rh-F resonance of [XIV], F_{3M} ($^2J_{C-F}$ = 64Hz) and the second was a 3 bond C-F coupling in the highest frequency S-F resonance of [XV], f_{3A} ($^3J_{C-F}$ = 24Hz). Thus we have assigned the three resonances, f_{3A}, $f_{3A'}$ and f_{3E} as arising from the complex;

[figure 3.3.7]



[XV]

We have assigned this complex as containing a chloride ligand rather than a second SCN ligand for the same reasons we gave in the discussion of the reaction of $Rh(CO)Br(PEt_3)_2$ with SF_4, namely the presence of CD_2ClF in the ^{19}F n.m.r. spectrum and no obvious evidence for a product of NCS abstraction from $Rh(CO)NCS(PEt_3)_2$ in the $^{31}P-\{^1H\}$ n.m.r. spectrum.

The $^{31}P-\{^1H\}$ n.m.r. spectrum for this complex was very difficult to assign: in the 81.015MHz spectrum the resonance lay under the B part of the ABQRSTX pattern arising from complex [XIV] and even at 145.875MHz only the a and b multiplets were unobscured by the ABQRSTX pattern of [XIV]. Therefore we were unable to calculate the positions of δP_A and δP_B, nor to obtain all the coupling constants for this complex.

On warming to 255K the two axial S-F resonances began to lose their couplings whilst the equatorial S-F resonance remained sharp but by 260K both the axial and equatorial S-F resonances had broadened considerably ($W_{½AX}$ = 450Hz) and lost all couplings. On further warming to 270K all three S-F resonances were no longer distinguishable from the baseline and if the reaction was warmed further, decomposition occurred.

As previously, observing the $^{31}P-\{^1H\}$ n.m.r. spectrum on warming, provided little information on the resonances arising from this complex.

The third most significant set of resonances observed in the $^{19}F-\{^1H\}$ n.m.r. spectrum at 195K were

seen in a 1:1:1 ratio at δ-72.1, δ-337.8 and δ-380.7. These are three of the resonances which we previously assigned as arising from the difluoride $-SF_3$ complex [VI]. These three resonances were observed at approximately 25% of the intensities of the resonances attributed to complex [XIV]. On warming, all three resonances behave in the same way as the same resonances which we observed in each of the previous reactions. The axial S-F resonances for this complex were not observed as they lay underneath the axial S-F resonances of complex [XIV].

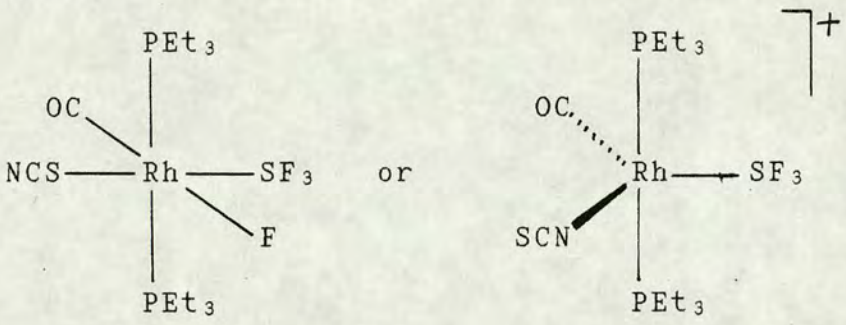
In the $^{31}P-\{^1H\}$ n.m.r. spectrum we could observe the resonance at δ36.5 but due to imposition of other resonances upon it we could extract no coupling information from it.

The next most significant resonances observed in the $^{19}F-\{^1H\}$ n.m.r. spectrum were observed at approximately 10% of the intensities of the resonances of complex [XIV]. These were four resonances, f_{3a}, $f_{3a'}$, f_{3e} and f_{3m} observed at δ77.1, δ45.9, δ-75.7 and δ-363.6 which were of approximately equal intensities.

These resonances were so weak that we were unable to resolve any fine couplings which would have helped us to assign the actual composition of this complex. On the basis of the relatively high chemical shift of the Rh-F resonance we have assigned this fluoride to be *trans* to CO rather than halide or pseudohalide and since the S-F resonances do not lie at

the same frequencies as those arising from complex [I] we assume that this complex [XVI] must be either the sulphur bonded SCN analogue of [XIV], E, or a 5-coordinate species, F;

[figure 3.3.8]



[XVI]E [XVI]F

On observation of the Rh-F region of the $^{19}F-\{^{1}H\}$ n.m.r. spectrum of the products of the reaction of $Rh(^{1.3}CO)NCS(PEt_3)_2$ with SF_4, the resonance at δ-363.6 was observed to broaden. However, all the S-F resonances which we already knew did not couple to ^{13}C were still very sharp, so although we did not resolve the $^{2}J_{C-F}$ from this resonance we feel that the fact this resonance has broadened is good evidence for our assignment of F being *trans* to CO. This, however, does not help us to assign the rest of the coordination positions of the rhodium.

In an attempt to gain more information the isotopically enriched $Rh(CO)SC^{15}N(PEt_3)_2$ starting material was prepared and reacted with SF_4. However, no change was seen in the $^{19}F-\{^{1}H\}$ or $^{31}P-\{^{1}H\}$ n.m.r. spectra. This fact is not surprising as ^{15}N normally couples very weakly to other nuclei[45]. Neither were we

able to observe the ^{15}N n.m.r. spectrum as the amount of sample required was too great.

We can, therefore, say very little about the full nature of this complex at present except that it contains a Rh(III) nucleus, an SF_3 group and CO and F bonded directly to rhodium.

Although the S-F resonances of this complex were weak we decided to observe its fluxionality. As the axial S-F resonances were sandwiched between the much more intense axial S-F resonances of [XIV] and [XV] this meant that we could only use the equatorial S-F and Rh-F resonances to do this.

At 250K the equatorial S-F resonance began to lose its couplings; this is a rather higher temperature than observed previously for complexes in which CO is *trans* to SF_3, affording further evidence that our structure is correct. Unfortunately, however, the broadening of the equatorial S-F resonance of [XVI] made it impossible for us to study the fluxionality to higher temperature and, indeed, the complex decomposed above 260K.

In the $^{31}P-\{H\}$ n.m.r. spectrum at 195K [figure 3.3.5] we could observe the a and b resonances of an ABQX pattern; the c and d resonances were obscured by other, more intense resonances. The intensity of the b resonance was approximately 10% of the intensity of the b resonance of the ABQRSTX pattern of [XVI]. As the $^{19}F-\{^1H\}$ n.m.r. spectrum showed only one complex around this intensity we have therefore assigned these two

resonances as being the a and b resonances of an AB type pattern arising from complex [XVI].

Table 3.3.5.

Chemical shifts for species [XVI]/p.p.m.

S-F			Rh-F
f_{3a}	$f_{3a'}$	f_{3e}	f_{3m}
77.1	45.9	-75.7	-363.6

Table 3.3.6.

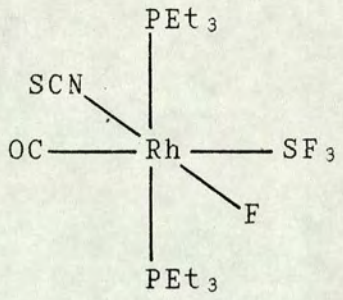
Coupling constants for Species [XVI]/Hz

Nuc.	f_{3a}	$f_{3a'}$	f_{3e}	f_{3m}	P_A	Rh
f_{3a}	-	179	65	n.o.	n.o.	n.o.
$f_{3a'}$	179	-	72	9	32	n.o.
f_{3e}	65	72	-	n.o.	n.o.	n.o.
f_{3m}	n.o.	9	n.o.	-	32	123
P_A	n.o.	32	n.o.	32	-	72

The $^1J_{P-Rh}$ coupling is consistent with a 6 coordinate Rh(III) centre which implies that the most likely structure is [XVI]E.

The final resonances observed in the $^{19}F-\{^1H\}$ n.m.r. spectrum were an equatorial S-F resonance at δ-65.0 and a Rh-F resonance at δ-402.2. Both had approximately equal intensities at around 20% of the intensities of the resonances arising from complex [XVI]. The S-F resonance began to broaden at 200K and on this basis and the low frequency of the Rh-F resonance we believe that these resonances probably arise from the isomer of complex [XIV], [XVII];

[figure 3.3.9]



[XVII]

The axial S-F resonances must be hidden underneath the other axial S-F resonances. Both observed resonances were too weak to resolve couplings and no corresponding ^{31}P resonances could be resolved.

3.4 Reaction of $Rh(CO)NCO(PEt_3)_2$ with SF_4.

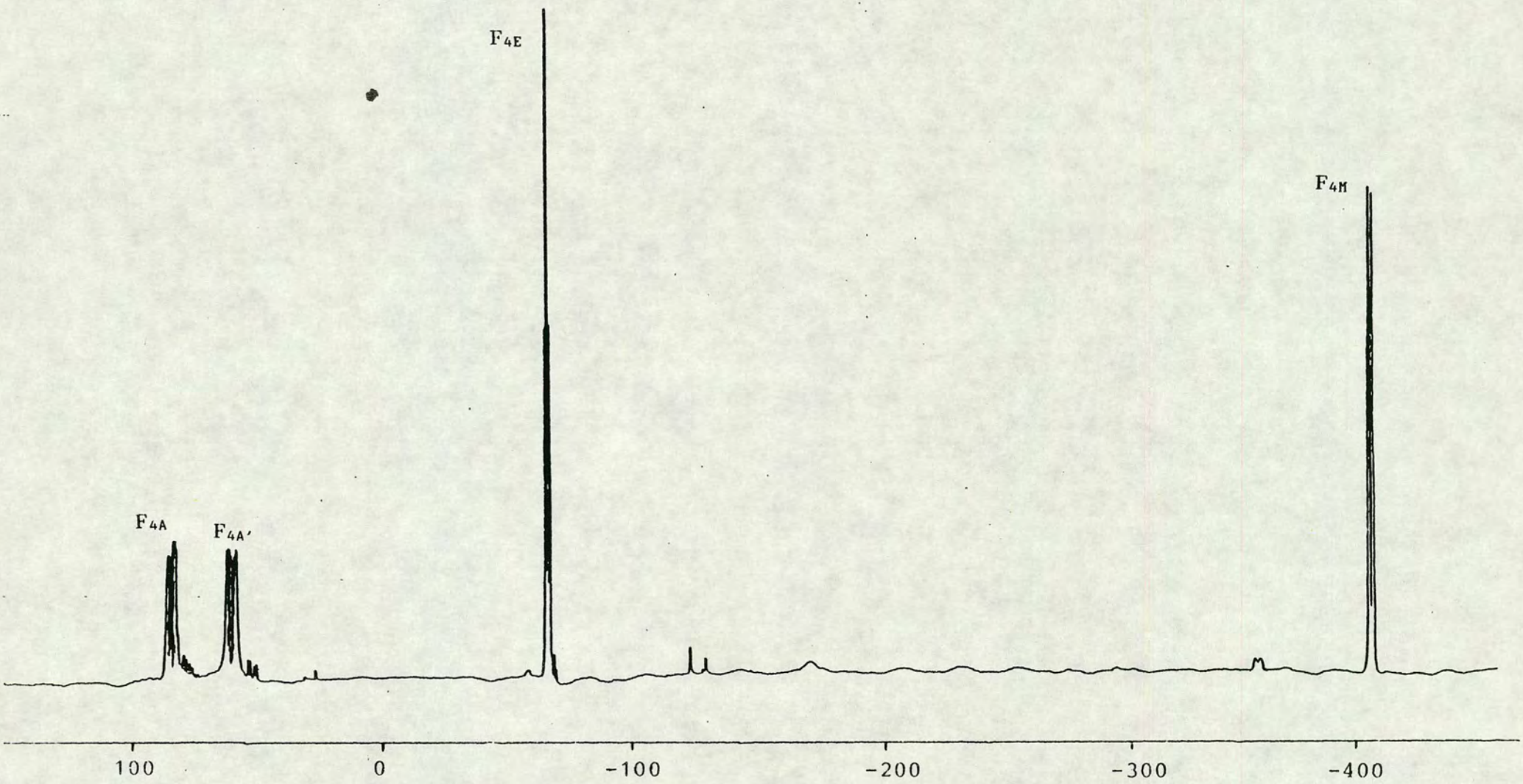
To extend our series of complexes to study, we prepared and reacted the cyanate analogue, $Rh(CO)NCO(PEt_3)_2$, with SF_4.

On melting, the solution became deep orange. The $^{19}F-\{^1H\}$ n.m.r. spectrum at 195K was rather susprising [figure 3.4.1]. We had expected to observe a spectrum similar to that observed in the $Rh(CO)NCS(PEt_3)_2$ reaction but, in fact, we observed the simplest spectrum of any reaction mixture yet studied. Only four resonances of significant intensity were observed; F_{4A}, $F_{4A'}$, F_{4E} and F_{4M}. These resonances were a doublet of doublets of doublets of doublets at δ83.1, a doublet of doublets of doublets of doublets of doublets at δ58.4, a doublet of doublets of doublets of triplets at δ-69.1 and a doublet of triplets of doublets at δ-401.3. Parameters are detailed in tables 3.4.1 and 3.4.2.

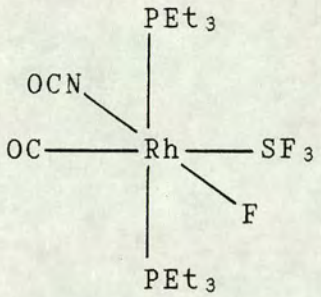
On comparison of these chemical shifts with those assigned previously to other $Rh-SF_3$ complexes we can see that the Rh-F resonance is at very low frequency suggesting that it is *trans* to a group more electron withdrawing than CO, namely NCO. Similarly, the S-F resonances are at relatively high frequency suggesting that they are *trans* to the CO ligand.

On this basis we have assigned this complex [XVIII] as having the isomeric form of all the previous major products;

Figure 3.4.1; $^{19}F - \{^{1}H\}$ nmr spectrum of $Rh(CO)NCO(PEt_3)_2$



[figure 3.4.2]



[XVIII]

Table 3.4.1.

Chemical Shifts for Species [XVIII]/p.p.m.

S-F			Rh-F	P
F_{4A}	$F_{4A'}$	F_{4E}	F_{4M}	P_A
83.1	58.4	-69.1	-401.3	27.4

Table 3.4.2.

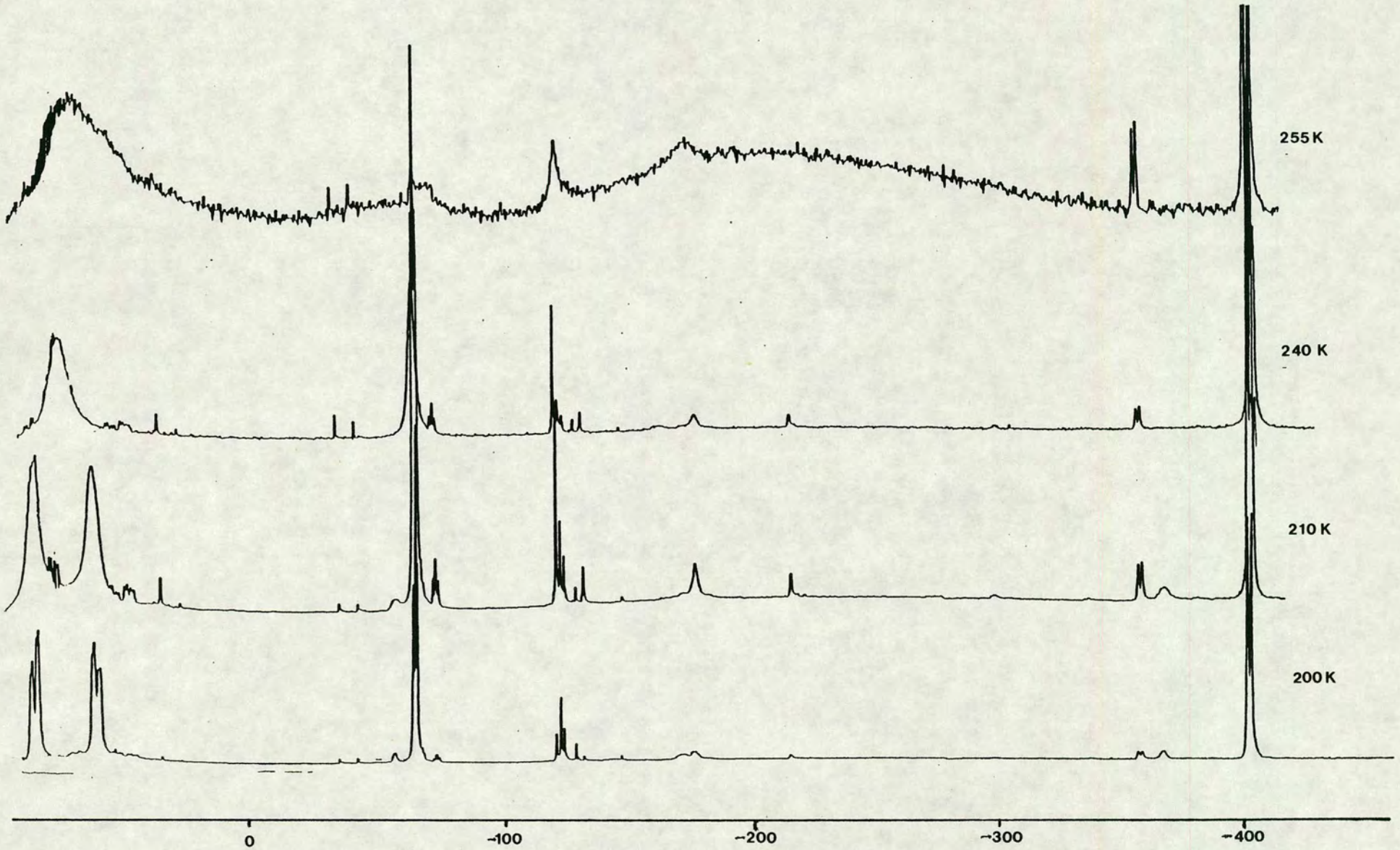
Coupling Constants for Species [XX]/Hz

Nuc.	F_{4A}	$F_{4A'}$	F_{4E}	F_{4M}	P	Rh
F_{4A}	-	187	67	n.o.	4	11
$F_{4A'}$	187	-	83	10	28	16
F_{4E}	67	83	-	n.o.	8	15
F_{4M}	n.o.	10	n.o.	-	28	114
P	n.o.	28	8	28	416	75

As previously, the $^{31}P-\{^1H\}$ n.m.r. spectrum was not very helpful as it only showed a broad resonance ($W_{½}$ = 160Hz) from which no couplings could be resolved.

On warming, the ^{19}F n.m.r. spectrum changed rather dramatically [figure 3.4.3]. At 200K the axial S-F resonances had lost all couplings save their mutual couplings. The Rh-F resonance at this temperature was

Figure 3.4.3; V.t. $^{19}F-\{^1H\}$ n.m.r. spectra of $Rh(CO)NCO(PEt_3)_2$ + SF_4 at 195K.



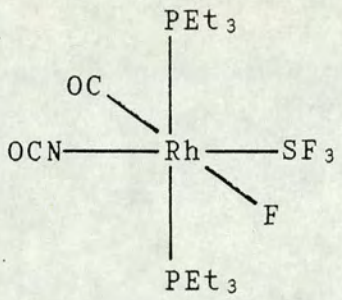
only a doublet. At 210K the axial S-F resonances had lost all couplings and the equatorial S-F resonance now began to lose its couplings. The Rh-F resonance now resharpened to a doublet of triplets, losing its coupling to the axial S-F. At 225K the axial S-F resonances had almost coalesced, forming a broad resonance ($W_{½}$ = 2000Hz) and the equatorial S-F resonance had become a broad triplet. At 240K the axial S-F resonances had now coalesced and the equatorial S-F resonance had broadened considerably. At 255K the coalesced axial S-F resonance was very broad ($W_{½}$ = 750Hz) and the equatorial S-F resonance was even more broad ($W_{½}$ = 1100Hz). By 270 K all three S-F resonances had disappeared, although the Rh-F resonance remained sharp. On recooling to 195K from this temperature all four resonances reappeared in their original form but on warming above 295K and recooling, decomposition was observed to have occurred.

As previously, the $^{31}P-\{^{1}H\}$ n.m.r. spectra were not very helpful on warming. At 225k the broad resonance became a broad doublet ($^{1}J_{P-Rh}$ = 71Hz). No further change was observed until the complex decomposed at 295K.

Also observed in the ^{19}F n.m.r. spectrum at 195K were four extremely weak resonances at δ74, δ45, δ-77 and δ-358. These resonances were too weak to resolve any couplings but due to the relatively high chemical shifts of the Rh-F resonance, implying that it was *trans* to CO and the relatively low chemical shifts of the S-F

resonances, implying SF_3 *trans* to halide or pseudohalide, we have assigned this complex as the isomer of [XVIII], [XIX];

[figure 3.4.4]



[XIX]

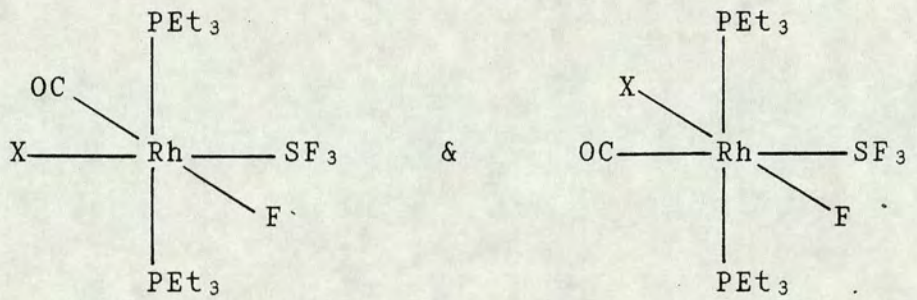
No resonance was observed in the $^{31}P-\{^{1}H\}$ n.m.r. spectrum for this complex.

3.5 Discussion.

Multinuclear n.m.r. spectroscopy has shown that, like their iridium analogue, the complexes $Rh(CO)X(PEt_3)_2$ [X = Cl, Br, I, NCS, NCO] react with SF_4 to form complexes containing the SF_3 ligand. However, in contrast to the iridium reaction, a variety of complexes are formed.

In all five reactions the two isomers;

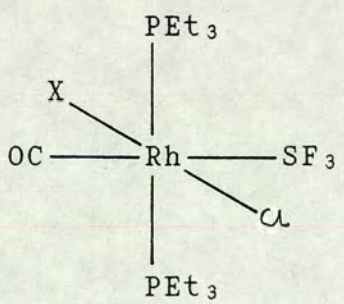
[figure 3.5.1]



[A] [B]

are formed. Also formed is the complex where the fluoride ligand has been replaced by a chloride (which we believe is a result of the fluoride reacting with solvent);

[figure 3.5.2]

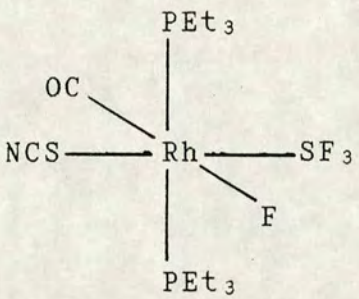


[C]

In all of the reactions, with the exception of the isocyanate reaction, we also observed the difluoride complex [VI].

Finally, in the reaction of $Rh(CO)NCS(PEt_3)_2$ with SF_4 we observed a fifth species which we have tentatively assigned as the linkage isomer of complex [XVI], namely

[figure 3.5.3]

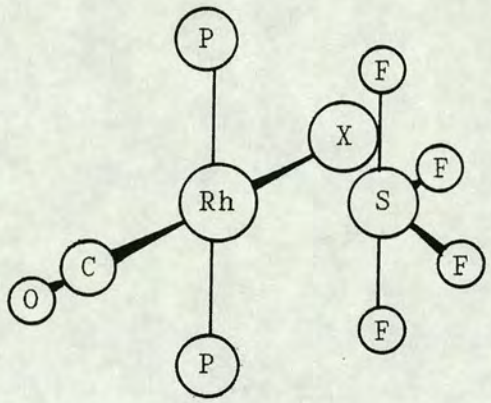


These complexes were formed in various ratios which were dependent upon X. If we ignore the cyanate reaction for the moment, as the major product in that reaction was different from the other four, the order for the ratio of [A]:[B] was

$$X = I > Br > Cl > NCS$$

The most likely explanation for this difference in the variation of the ratios of products is the steric effect that X has on the reacting SF_4 molecule. This is simply seen in the following diagram;

[figure 3.5.4]



If X is large then we can see that the sulphur is likely to be repelled by the X so that it is more likely to add *trans* to X. However, if X is small then the sulphur could add either *cis* or *trans* to X. Therefore in the reaction of $Rh(CO)Cl(PEt_3)_2$ with SF_4 we have several, relatively abundant, products but in the analogous reaction where Cl has been replaced by the larger iodide ligand we see only one particularly abundant product. This argument also holds for the isothiocyanate reaction as we know that the NCS group is bound by the small nitrogen end in the starting material. It does not, however explain why only one major product is observed in the reaction of the isocyanate starting material with SF_4, as we would expect a similar ratio of products as we observed in the isothiocyanate reaction, but it does account for the fact that the sulphur is *cis* to the NCO group.

The fluxionalities of these complexes also varied depending upon the nature of X.

For each complex, on warming, we saw the axial S-F resonances gradually lose their couplings, broaden

and in some cases coalesce. As they lost their couplings we observed the equatorial S-F resonance also lose its couplings and then broaden, whilst the Rh-F resonance broadened and resharpened having lost its coupling to the low frequency axial S-F. If the tube was recooled before decomposition occurred the original spectrum was again observed, indicating that the process we had observed was reversible.

These results indicate that one of two processes was occurring;

i) Intermolecular exchange or

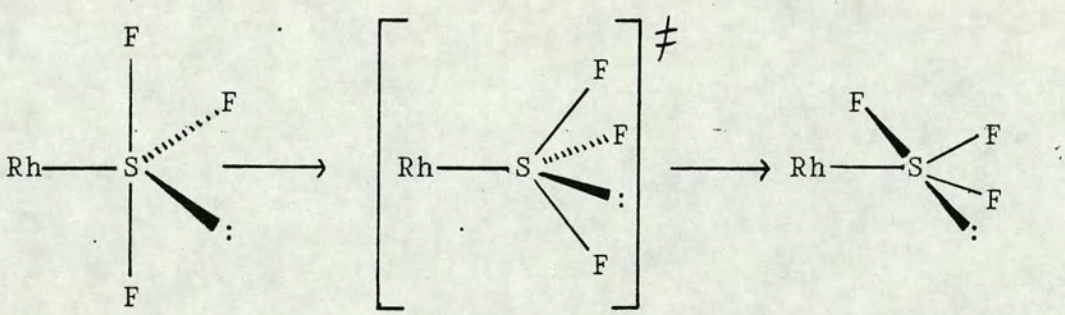
ii) Intramolecular exchange.

Since in those complexes which do not decompose before both axial S-F's become equivalent, and in the analogous iridium system, we observe the equatorial S-F resonance resharpening to a triplet ($^2J_{F-F}$) we conclude that the fluxional process we have been observing is intramolecular exchange.

Therefore, we propose that the changes observed in the n.m.r. spectra on warming are the result of an intramolecular exchange process which becomes faster as temperature is increased so that at a particular temperature both axial S-F's become equivalent, whilst the equatorial S-F remains distinct. This process is most likely a rocking or rotation about the Rh-S bond. Since the equatorial S-F resonance remains distinct, pseudorotation at sulphur cannot be involved. A similar process was also seen in the analogous $Ir(CO)Cl(PEt_3)_2$

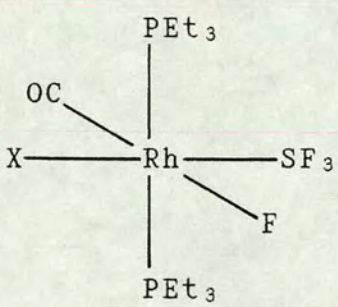
reaction[43]. In that case, as in that of the difluoride complex [VI], the complex could be studied to higher temperature as decomposition did not occur. Heating above the temperature at which the axial S-F's became equivalent, lead to coalescence of all three S-F resonances at a chemical shift which was the average of their initial chemical shifts, whilst the metal fluoride resonance lost its coupling to the low frequency axial S-F, keeping its coupling to Rh. This showed that the SF_3 group was undergoing Berry-pseudorotation[62] where all three S-F's were interchanging;

[figure 3.5.5]



If we compare the fluxionalities of the complexes;

[figure 3.5.6]



[X = Cl, Br, I, NCS]

[1]

we have observed that the fluxionality varies with X such that the order of fluxionality is

X = I < Br ≃NCS < Cl < F

There are two likely reasons for this difference in fluxionality;

i) electronic effects or

ii) steric effects.

Although the dπ orbitals of Rh(III) are formally filled we would still expect some π-donation and π-acceptance to occur between the ligand orbitals and the Rh d orbitals. As in SF_4, we may expect that the SF_3 group will have both Lewis acid and Lewis base character[4]. Thus we can assume that there may be a certain amount of π-interaction between the filled dπ orbitals of rhodium and the empty d orbitals of sulphur. The stronger this interaction is then the less facile would be rotation about the Rh-S bond. Consequently, if the *trans* ligand is a π-acceptor it would remove electron density from rhodium, decreasing the amount of d-d π-interaction and thus facilitating rotation about the rhodium-sulphur bond. Conversely, if the *trans* ligand is a π-donor then it would donate more electron density to rhodium, increasing the d-d π-interaction between rhodium and sulphur and thus inhibiting rotation about the rhodium-sulphur bond.

However, if this were the case, we would expect X = Cl to be the least fluxional complex and X = I to be

the most fluxional as chloride is a better π-donor ligand than iodide as the d orbitals of iodide are very diffuse leading to poor overlap. This is, of course, the opposite to what we observe.

If steric effects were responsible for the difference in fluxionality then it is the *trans* ligand which is responsible for the change. This may at first seem unlikely. However, we have seen from the x-ray crystal structure of $Rh(CO)NCS(PEt_3)_2$ that the alkyl groups of the phosphines are in relatively close contact with the other ligands and so we may expect that as the size of X is increased there will be a larger influence on the alkyl groups of the phosphines which may then cause interaction with the *trans* SF_3 group.

This steric argument is the most likely explanation for the difference in fluxionality of these complexes

In an attempt to shed some light on the likelihood of this steric hindrance affecting the fluxionality of the SF_3 group some simple molecular mechanics experiments were performed using the MM2 program[63].

The single crystal x-ray crystal structure of $Ir(CO)ClF(PEt_3)_2SF_3$ was reported[43] but the SF_3 group was observed to be disordered. The results of this structure were taken and estimated bond angles and bond lengths for the SF_3 group were added and a steric energy minimisation calculation was performed[64]. The resulting

structure is shown as a space-filled diagram in figure 3.5.7.. Then, the dihedral angle P-Ir-S-F_{AX} was fixed at 0° (this angle is the one where we would expect most steric hindrance between the phosphine groups and the SF_3 group) and the complex was allowed to minimise sterically. The result of this minimisation is shown in figure 3.5.8.

Obviously if the SF_3 group undergoes a rotation about the Rh-S bond then the complex must pass through both of these configurations.

If we compare both structures we can see that overall there is little difference between them, apart from the obvious SF_3 group. However, in the areas marked in red we see a small, but we believe significant, change in the orientation of the ethyl groups of the PEt_3 ligands.

We thus conclude that the orientation of the SF_3 group influences the positions of the phosphine's ethyl groups and so, conversely, the positions of the ethyl groups will influence the movement of the SF_3 group. Therefore this steric calculation supports our proposition that the size of the X group in these complexes is the most important factor in determining the fluxionality of the SF_3 group.

The second series of complexes we have observed were those of the form;

Figure 3.5.7

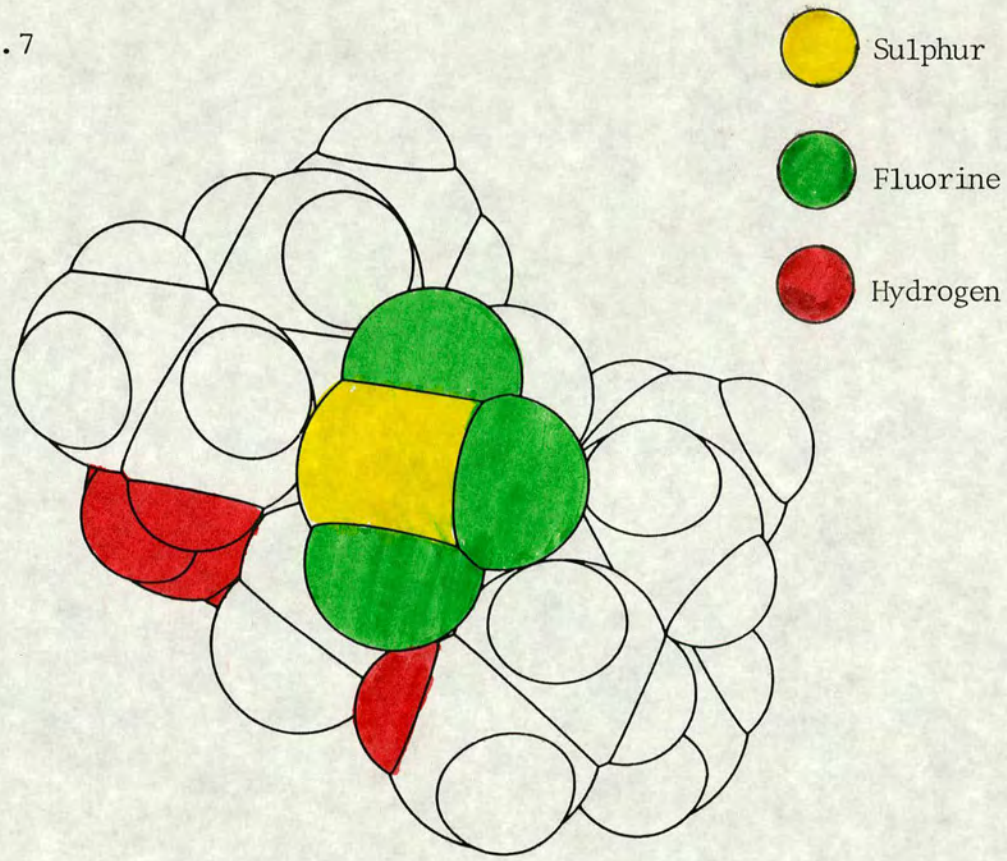
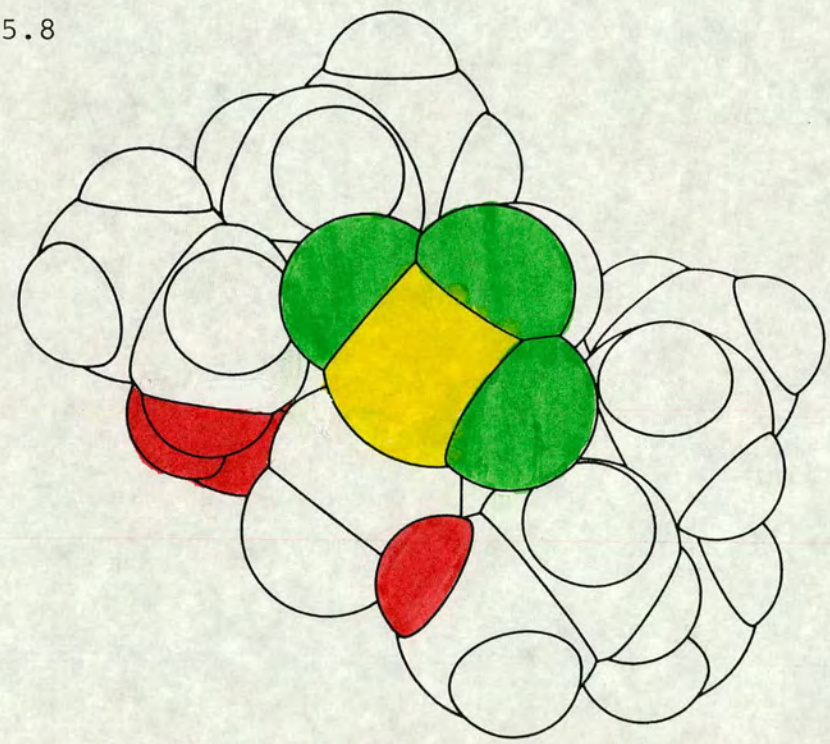
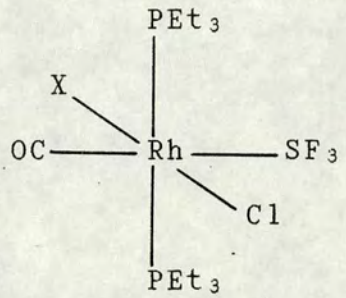


Figure 3.5.8



[figure 3.5.9]



[2]

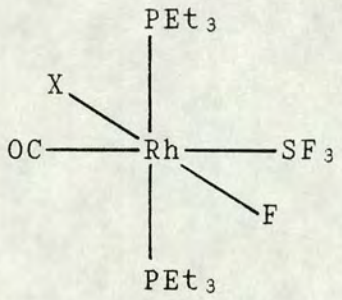
In these complexes the fluxionality also varies with X such that the fluxionality increases as the size of X increases;

X = NCS < Cl < Br < I

Here the fluxionality increases as X gets larger, the opposite effect to that previously discussed. The obvious explanation, however is essentially the same as before. The larger X is , the more it will repel the phosphines, but in this complex X is *cis* to SF_3 and so, in effect, the large X will push the ethyl groups away from the SF_3 group allowing easier rotation about the Rh-S bond.

The third series of complexes observed was the isomers of the first set of complexes discussed;

[figure 3.5.10]



[X = Cl, Br, NCS, NCO]

[3]

We cannot compare the fluxionalities of these complexes however as they all, apart from where X = NCO, were so weak.

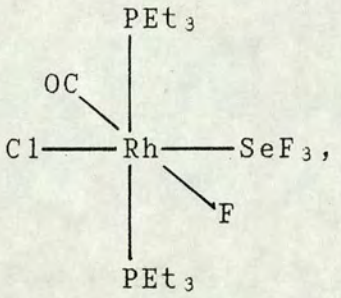
If we compare the three types of complex we see that the order of fluxionality is;

Type = [1] < [2] < [3]

Our argument about the significance of the size of the *trans* ligand can explain why [1] is less fluxional than [2] and [3] as halide will be larger than carbon, except that when X = NCS, nitrogen is smaller than carbon and so the NCS complex should be the most fluxional, which we know it is not. Therefore, we propose that the difference in fluxionality between these complexes is due to the electronic factors discussed earlier in this section i.e. those complexes with halide *trans* to SF_3 are less fluxional than those which have CO *trans* to SF_3 as a result of a small, but significant amount of π back-bonding between rhodium and sulphur.

Chapter Four.

Key to Structures and Numbers in Chapter 4.



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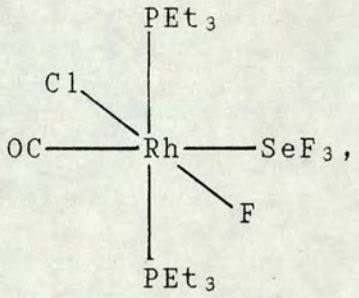

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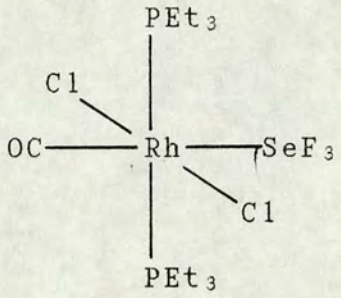

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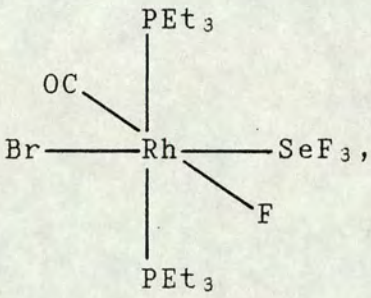

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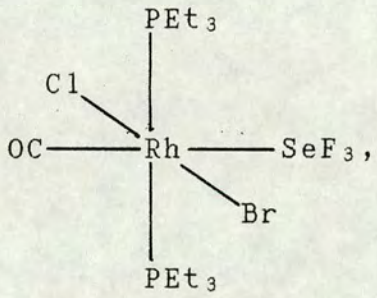

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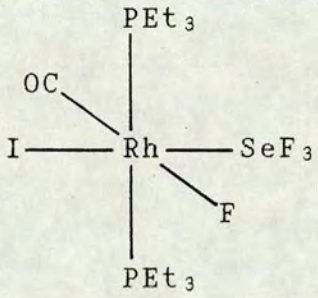

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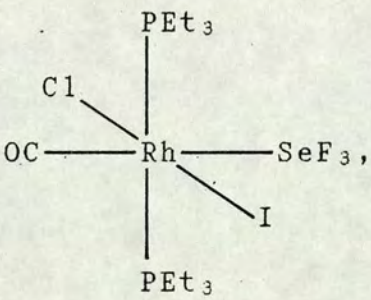

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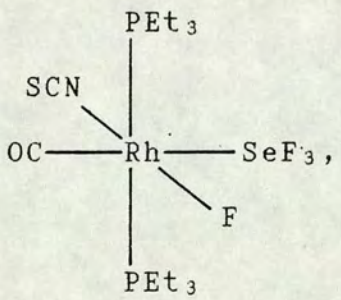

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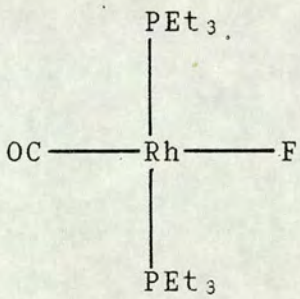

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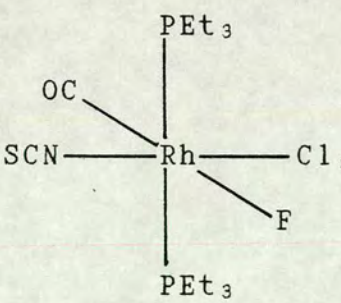

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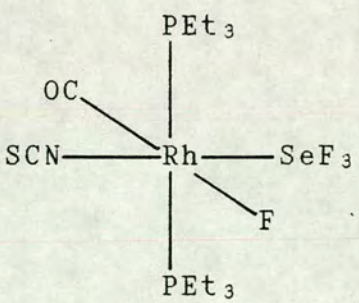

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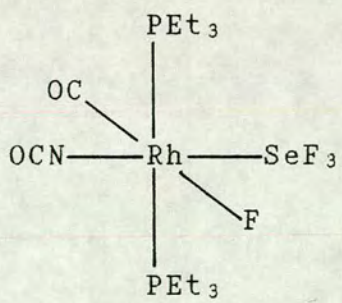

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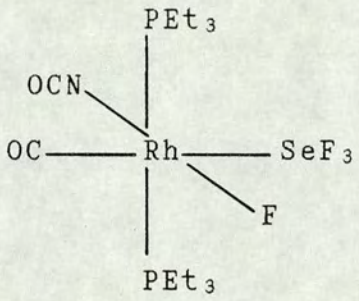

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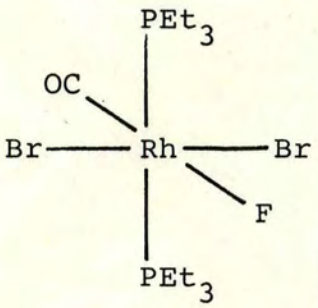


[XLIV]

Reactions of SeF_4.

Since SF_4 and SeF_4 have generally similar chemistries it was decided to react SeF_4 with the complexes $Rh(CO)X(PEt_3)_2$ [X = Cl, Br, I, NCS, NCO] in an attempt to form complexes containing the novel SeF_3 ligand.

The reactions were carried out in F.E.P. tubes, rather than n.m.r. tubes, as SeF_4 reacts readily with glass if a trace of moisture is present. This caused some problems with resolution and a wavy baseline was observed in the $^{19}F-\{^1H\}$ n.m.r. spectra due to fluorine in the F.E.P. but generally well resolved, high quality spectra were obtained.

4.1 Reaction of $Rh(CO)Cl(PEt_3)_2$ with SeF_4

At 195K the $^{19}F-\{^1H\}$ n.m.r. spectrum was very similar to those observed in the analogous sulphur systems [figure 4.1.1]. Several resonances were observed. The most intense were four resonances F_A, $F_{A'}$, F_E and F_M of approximately equal intensities. These were a doublet of doublets of doublets of doublets at δ8.3, a doublet of doublets of doublets of doublets of doublets at δ-10.6, a doublet of doublets of doublets of triplets at δ-103.7 and a doublet of triplets of doublets at δ-373.4. Parameters are detailed in tables 4.1.1 and 4.1.2 and expansions of all four resonances are given in figures 4.1.2 and 4.1.3.

The resonance at δ-373.4 is in the correct region of the spectrum for a fluoride which is bonded to a Rh(III) nucleus and which is also *trans* to a carbonyl group. The other three resonances are all at significantly lower frequencies than the ^{19}F resonances of the SF_3 groups observed in the analogous sulphur systems. However, their multiplicities are identical to those observed in the $Rh-SF_3$ systems. This result is consistent with what is observed in organic systems as the ^{19}F chemical shifts of alkyl-SeF_3 compounds are observed at significantly lower frequencies than those of the analogous sulphur compounds[65]. This is not surprising as we would expect the fluorine nuclei in an SeF_3 group to be more shielded than those in an SF_3 group and thus occur at lower frequency. The resonance at δ-103.7 also had ^{77}Se

Figure 4.1.1; $^{19}F-\{^{1}H\}$ n.m.r. Spectrum of $Rh(CO)Cl(PEt_3)_2$ + SeF_4 at 195K

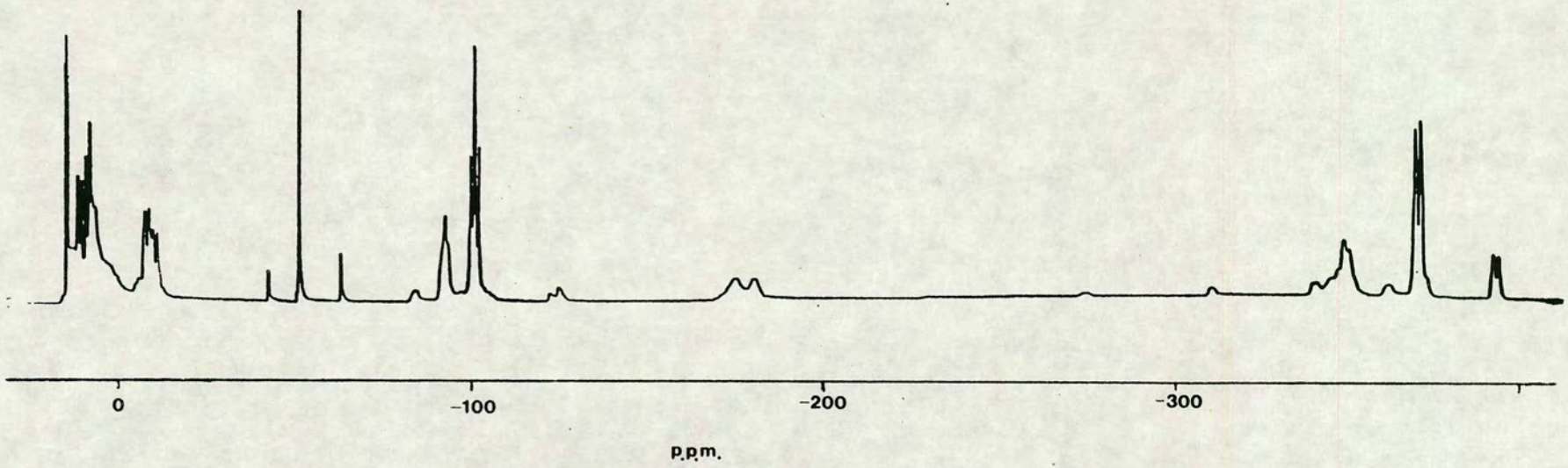


Figure 4.1.2; Expansions of F_A & $F_{A'}$

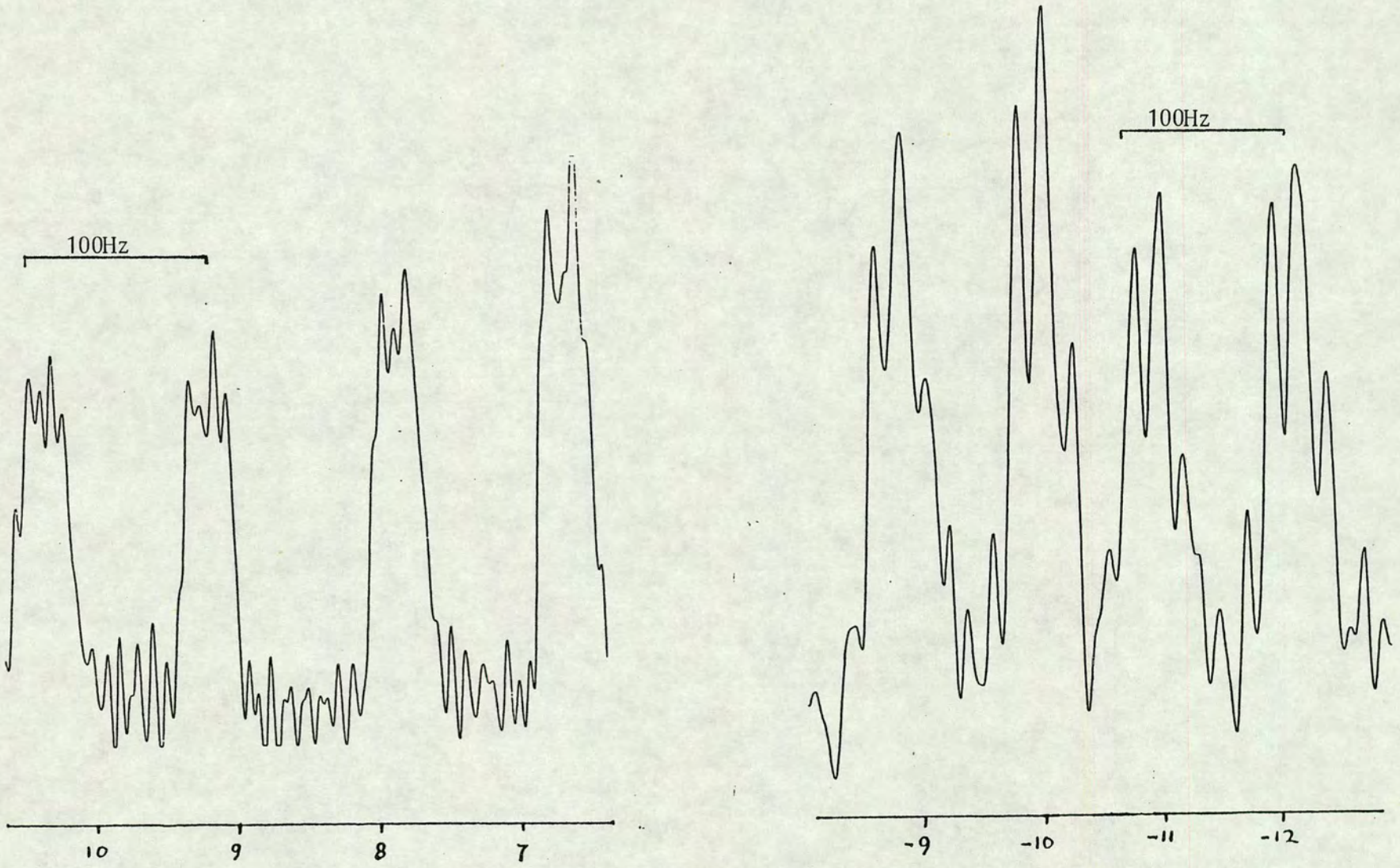
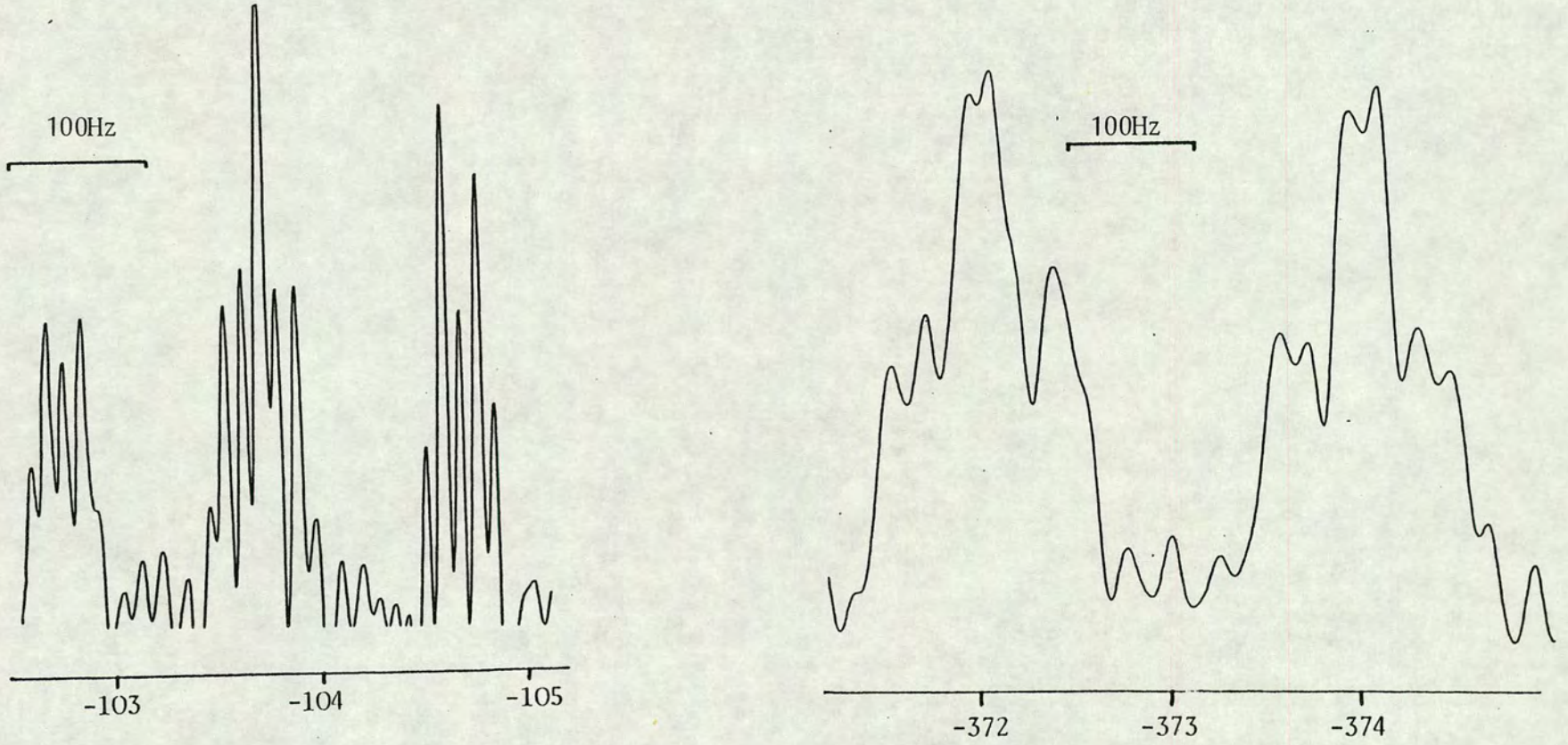
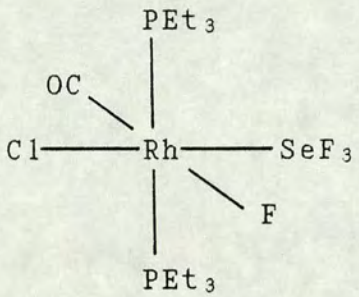


Figure 4.1.3; Expansions of F_E & F_M



satellites at approximately 4% of the intensity of the resonance ($^1J_{F-Se}$ = 580Hz).

On this basis we have assigned these four resonances as arising from the novel complex [XX]; [figure 4.1.4]



[XX]

Table 4.1.1.

Chemical Shifts for Species [XX]/p.p.m.

Se-F			Rh-F	P
F_A	$F_{A'}$	F_E	F_M	P
8.3	-10.6	-103.7	-373.4	29.9

TABLE 4.1.2.

Coupling Constants for Species [XX]/Hz

Nuc.	F_A	$F_{A'}$	F_E	F_M	P	Rh
F_A	-	172	82	n.o.	6	11
$F_{A'}$	172	-	95	14	20	19
F_E	82	95	-	n.o.	7	14
F_M	n.o.	14	n.o.	-	27	114
P	6	20	7	27	-	n.o.

Unfortunately, when these experiments were performed the decoupler on the 200MHz n.m.r. spectrometer was not functioning properly and consequently the 81.015MHz $^{31}P-\{^{1}H\}$ n.m.r. spectra obtained were not of sufficient resolution to obtain any couplings other than $^{2}J_{P-P}$.

On observation of the 145.875MHz $^{31}P-\{^{1}H\}$ n.m.r. spectrum at 195K we observed an AB pattern in which all four resonances a, b, c and d were very broad. It is unlikely that this broadening is due to chemical shift anisotropy, as we have always previously seen at least $^{1}J_{P-Rh}$ at this field. This broadening is more likely to be due to poor resolution as a result of not shimming on an internal lock.

On warming, the $^{19}F-\{^{1}H\}$ n.m.r. spectrum of [XX] changed in a manner which suggested fluxional behaviour. At 215K the two axial Se-F resonances began to lose their couplings and broaden even more. The equatorial Se-F resonance remained unchanged but the Rh-F resonance began to broaden further, showing only a doublet coupling ($^{1}J_{F-Rh}$). At 225K the axial Se-F resonances had broadened considerably, showing only their mutual couplings; the equatorial Se-F resonance was still sharp at this temperature and the Rh-F resonance had broadened further. At 235K both axial Se-F resonances had disappeared and a new resonance had appeared at δ1.4. This was a broad ($W_{½}$ = 550Hz), unresolved peak whose intensity was twice that of the still sharp equatorial Se-F resonance. We have assigned

this peak as the resonance arising from two equivalent axial Se-F resonances of complex [XX]. This assignment was made on the basis of the integral and the chemical shift which is very close to the average value of the chemical shifts of F_A and $F_{A'}$. Also, the equatorial Se-F resonance had changed to a triplet ($^2J_{F-F}$ = 89Hz) indicating coupling to two equivalent Se-F's. The Rh-F resonance had resharpened at this temperature to a doublet of triplets, losing its coupling to $F_{A'}$.

These results are very similar to those observed in the analogous sulphur reactions. Thus, we can conclude that the phenomenon causing these observations is a rocking or rotation of the SeF_3 group around the Rh-S bond.

On further warming to 255K the axial Se-F resonance had sharpened slightly ($W_{½}$ = 350Hz) and begun to show signs of coupling. The equatorial Se-F and Rh-F resonances remained unchanged at this temperature. At 270K the axial Se-F resonance had sharpened to a doublet ($^2J_{FA-FE}$ = 89Hz), the equatorial Se-F resonance was still a sharp triplet of the same coupling and the Rh-F resonance was still a sharp doublet of triplets. On warming to 290K the Se-F region of the spectrum was unchanged, but the Rh-F resonance had lost all couplings and had broadened considerably. The most likely explanation for this is intermolecular fluoride exchange, although no HF resonance was observed in the expected region of the spectrum.

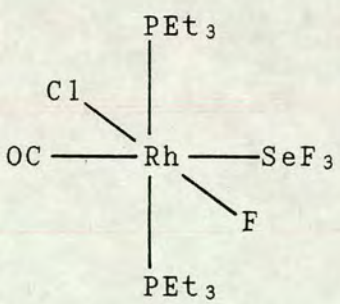
We did, however observe two resonances at 195K, a quintet at δ56.1 and a doublet at δ13.0 which were in the ratio 1:4, the intensity of the quintet was 20% of that of the Rh-F resonance of [XX]. The coupling constant of the quintet was the same as that of the doublet ($^2J_{F-F}$ = 30Hz) and we have thus assigned these resonances as arising from an SeF_5 group. The lack of other couplings meant that this group was not coordinated to Rh. Several compounds of the type SeF_5X have been reported[66-68] but they all have $^2J_{F-F}$ between 220 and 240Hz. We therefore propose that these resonances arise from the pentafluoroselenate(IV) anion SeF_5^-. This species is known[69,70], although its ^{19}F n.m.r. spectrum has not been reported. The ^{19}F n.m.r. spectra of a number of TeF_5^- species have been studied[71,72] and these show that $^2J_{F-F}$ in TeF_5X varies from 175 to 205Hz but that in TeF_5^- it is 50Hz.

These resonances broadened at the same temperature at which the Rh-F resonance of [XX] did. Therefore it is likely that there is intermolecular exchange of fluoride between $Rh(CO)ClF(PEt_3)_2SeF_3$ and SeF_5^- occurring at high temperature. If the tube is recooled from 290K the original spectrum is observed indicating that the intermolecular exchange is reversible. The complex was observed to decompose at 305K. The decomposition products included Et_3PF_2, CH_2ClF, HF and the monofluoride complex [VIII].

Also observed in the $^{19}F-\{^1H\}$ n.m.r. spectrum at 195K were four resonances f_A, $f_{A'}$, f_E and f_M which

were all at approximately equal intensities and occurred at δ11.8, δ-7.8, δ-93.7 and δ-395.7. All four resonances were approximately 25% of the intensities of each resonance of [XX]. The two highest frequency resonances were very broad, as was the Rh-F resonance, but the resonance at δ-93.7 was a well resolved triplet ($^2J_{F-F}$ = 74Hz). On warming to 200K the only change observed was that the Rh-F resonance had resolved into a doublet ($^1J_{F-Rh}$ = 115Hz). On further warming to 215K the two high frequency resonances had disappeared and a new resonance was observed at δ4.6. This resonance was a doublet ($^2J_{F-F}$ = 88Hz) and was at approximately twice the intensity of f_E, so we have assigned this doublet as the coalesced resonance of f_A and $f_{A'}$ which means that we are observing resonances from a second Rh-SeF_3 complex. We have assigned the Rh-F resonance as being *trans* to Cl due to its low chemical shift and thus we propose that the four resonances f_A, $f_{A'}$, f_E and f_M arise from complex [XXI];

[figure 4.1.5]



[XXI]

On further warming to 235K the Rh-F resonance again broadened, and no other change was observed in the

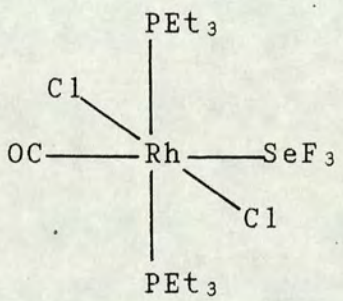
spectrum until 270K when the Rh-F resonance was no longer visible. The other three resonances were unchanged at this temperature and on recooling to 200K the Rh-F resonance again appeared as a doublet, although the intensities of all four resonances relative to those of [XX] was only half what it had been. This result suggests that the Rh-F is undergoing intermolecular exchange above a certain temperature. It is unlikely that this exchange involves the pentafluoroselenate(IV) anion, as the resonances belonging to this were still sharp up to 270K. More likely is that the exchange involves HF, as the characteristic resonance for this was observed at δ-183. These results imply that [XXI] is thermally less stable than than its isomer [XX]. It is also more fluxional, which is what we would predict, based upon our discussion of the analogous sulphur system. We have also seen that the Rh-F in complex [XX] appears to be more reactive than the analogous fluorides in the sulphur systems, and in complex [XXI] the Rh-F is even more reactive.

No ^{31}P resonance was observed for this species in the $^{31}P-\{^{1}H\}$ n.m.r. spectrum at any temperature. This is not surprising as we know that the spectrum is poorly resolved; it is also likely that any resonances would lie under the much more intense resonances of complex [XX].

Also observed in the $^{19}F-\{^{1}H\}$ n.m.r. spectrum at 195K was a third triplet, f_e, at δ-97.9 ($^{2}J_{F-F}$ =

68Hz). However, no Rh-F or axial Se-F resonances were observed which had intensities corresponding to that of this resonance. On warming to 215K a new resonance was observed, f_a, at δ10.3 which was a doublet ($^2J_{F-F}$ = 68Hz) at approximately twice the intensity of f_e. We have assigned these two resonances as arising from a third SeF_3 complex and due to the absence of a corresponding Rh-F resonance and the relatively high chemical shifts we have tentatively assigned the complex the structure;

[figure 4.1.6]



[XXII]

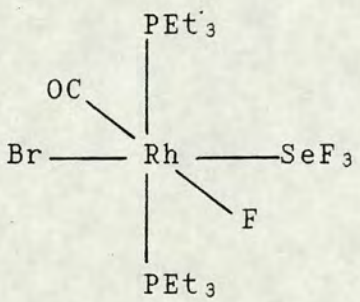
A significant amount of CH_2ClF was observed in the ^{19}F n.m.r. spectrum at δ-176.4 which is consistent with this assignment based on results discussed previously on the analogous sulphur systems. This complex decomposed at 250K.

4.2 Reaction of $Rh(CO)Br(PEt_3)_2$ with SeF_4

At 195K the $^{19}F-\{^1H\}$ n.m.r. spectrum showed several resonances [figure 4.2.2]. The most intense were four resonances F_{1A}, $F_{1A'}$, F_{1E} and F_{1M} which we observed as a doublet of doublets of doublets of doublets at δ6.1, a doublet of doublets of doublets of doublets of doublets at δ-10.7, a doublet of doublets of doublets of triplets at δ-104.0 and a doublet of triplets of doublets at δ-361.2. The resonance at δ-104.0 also had ^{77}Se satellites ($^1J_{P-Se}$ = 598Hz). Parameters are detailed in tables 4.2.1 and 4.2.2.

On the basis of this data and comparison with analogous systems we have assigned these resonances as arising from complex [XXIII];

[figure 4.2.1]



[XXIII]

The 81.015MHz $^{31}P-\{^1H\}$ n.m.r. spectrum at this temperature was as broad and unhelpful as that of the analogous chloride system, but we did obtain a well-resolved 145.875MHz spectrum which we observed as an ABX pattern in which the A parts showed evidence for further coupling; we could not determine this coupling.

Figure 4.2.2; $^{19}F-\{^{1}H\}$ n.m.r. Spectrum of $Rh(CO)Br(PEt_3)_2$ + SeF_4 at 195K

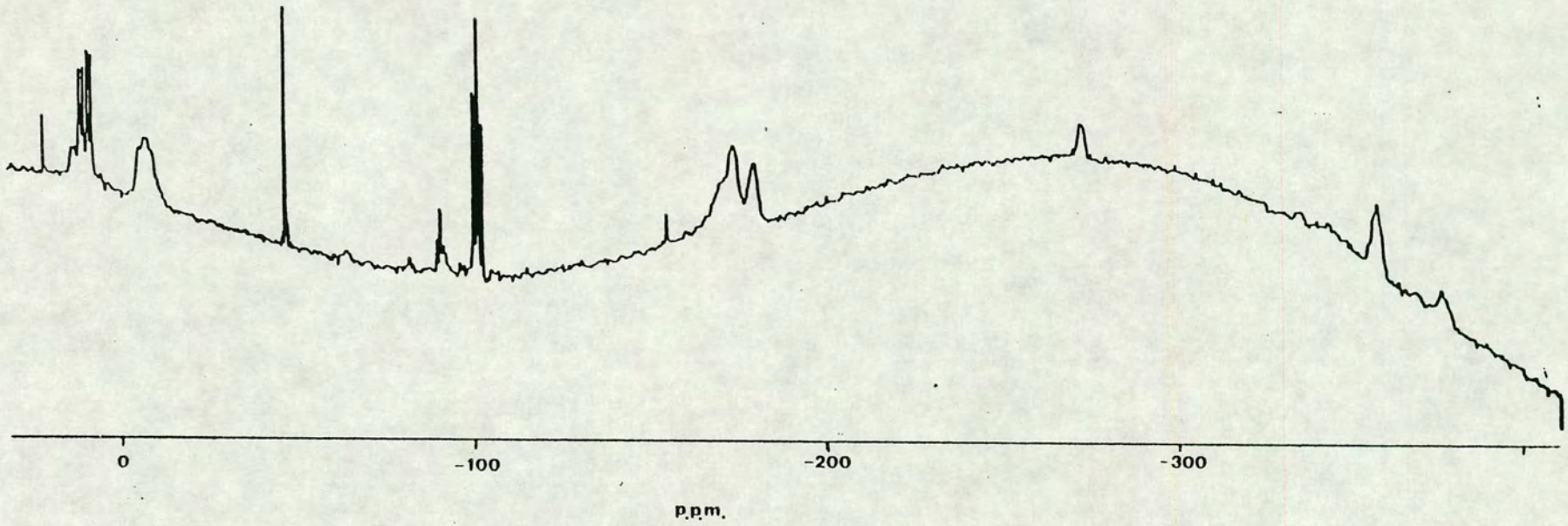


Table 4.2.1

Chemical Shifts for Species [XXIII]/p.p.m.

Se-F			Rh-F	P	
F_{1A}	$F_{1A'}$	F_{1E}	F_{1M}	P_A	P_B
6.1	-10.7	-104.0	-361.2	23.8	34.3

Table 4.2.2

Coupling Constants for Species [XXIII]/Hz

Nuc.	F_{1A}	$F_{1A'}$	F_{1E}	F_{1M}	P	Rh
F_{1A}	-	175	87	n.o.	6	10
$F_{1A'}$	175	-	97	10	20	18
F_{1E}	87	97	-	n.o.	7	13
F_{1M}	n.o.	20	n.o.	-	25	115
P	6	20	7	25	-	73

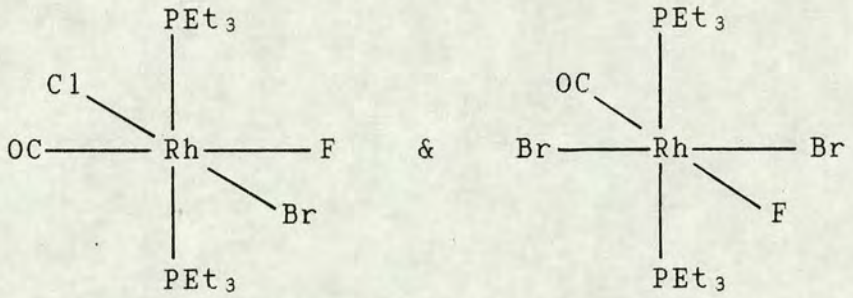
On warming, the ^{19}F spectra once again changed in a manner which suggested fluxional behaviour. At 210K the only difference in these four resonances was in the Rh-F resonance which had broadened. On further warming to 225K the only change observed was that the Rh-F resonance had resharpened considerably. As the other three resonances were fairly well resolved this means that the broadness of the Rh-F resonance was not a machine artefact but was a genuine broadening due to a chemical process. The most likely cause of broadening and then sharpening is that as the temperature increased the exchange process became fast on the n.m.r. timescale. At 240K the only change observed was again in the Rh-F resonance which had sharpened even further and had resolved into a doublet ($^1J_{F-Rh}$ = 73Hz). This means

that the previously observed fluxional process cannot involve the Rh-F, otherwise no coupling to Rh would have been observed in the Rh-F resonance. The most likely reason for the broadening of this resonance is either that the bromide or carbonyl ligands were undergoing intermolecular exchange or else they were exchanging with each other i.e. the complex was undergoing intramolecular isomerisation. If this is the case then we must assume that the equilibrium constant for this process is very small as we would expect to observe two sets of Se-F and Rh-F resonances but in fact only observe one set.

On further warming to 255K the Rh-F resonance had sharpened further and both axial Se-F resonances had broadened considerably ($W_{\frac{1}{2}}$ = 400Hz) although the equatorial Se-F resonance had remained sharp. On recooling to 195K from this temperature the same spectrum as previously was observed.

At 270K the complex was observed to have decomposed. Several broad Rh-F resonances were observed, one of which we had observed in the analogous SF_4 reaction and another which had been previously reported[52];

[figure 4.2.3]



[XI] [XLIV]

We also observed a very intense resonance due to HF. Presumably, the reason that these Rh-F resonances were broad was due to intermolecular exchange with HF.

The $^{31}P-\{^{1}H\}$ n.m.r. spectrum on warming showed the AB pattern collapsing and coalescing to a single broad resonance at δ28.7 from which no couplings could be resolved.

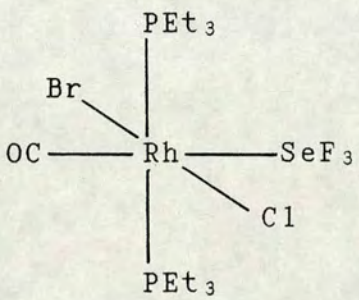
Also observed in the $^{19}F-\{^{1}H\}$ n.m.r. spectrum at 195K was a very weak triplet, f_{1E}, at δ-91.8 which was at approximately 10% of the intensity of the equatorial Se-F resonance of complex [XXIII]. There was evidence for axial Se-F resonances as we could observe small shoulders on the high frequency sides of the axial Se-F resonances of [XXIII], but we cannot positively assign these shoulders as being the corresponding axial Se-F resonances of a second SeF_3 group containing f_{1E}. No corresponding Rh-F resonance was observed.

A small broad doublet was observed in the $^{31}P-\{^{1}H\}$ n.m.r. spectrum at δ30.3 ($^{1}J_{P-Rh}$ = 70Hz) at approximately 10% of the intensity of the AB pattern arising from [XXIII]. As this was the only resonance

observed in the expected region at the correct intensity we have assigned this resonance tentatively as the corresponding ^{31}P resonance to the ^{19}F resonance f_{1E}.

On the basis of this small amount of information we have assigned these resonances as arising from a second SeF_3 complex, [XXIV];

[figure 4.2.4]



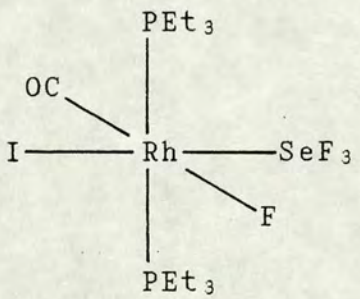
[XXIV]

On warming, the triplet did not change until 260K when it disappeared and did not reappear on cooling, indicating that decomposition had occurred.

4.3 Reaction of $Rh(CO)I(PEt_3)_2$ with SeF_4

At 195K the $^{19}F-\{^1H\}$ n.m.r. spectrum showed several resonances [figure 4.3.2]. The most prominent were four resonances of approximately equal intensities, F_{2A}, $F_{2A'}$, F_{2E} and F_{2M} at δ9.4, δ-9.9, δ-103.4 and δ-358.3. Only the 2-bond F-F couplings could be resolved in the Se-F resonances. In the Rh-F resonance no coupling at all was observed. This is likely to be due to intermolecular fluorine exchange, and it is also possible that this exchange is responsible for the loss of resolution in the Se-F resonances. On the basis of the chemical shifts and the coupling constants we did observe we have assigned these resonances as arising from the complex [XXV];

[figure 4.3.1]



[XXV]

Table 4.3.1

Chemical Shifts for Species [XXV]/p.p.m.

Se-F			Rh-F	P
F_{2A}	$F_{2A'}$	F_{2E}	F_{2M}	P
9.4	-9.9	-103.4	-358.3	28

Figure 4.3.2; ^{19}F $\{^{1}H\}$ n.m.r. spectrum of $Rh(CO)I(PEt_3)_2$ + SeF_4 at 195 K

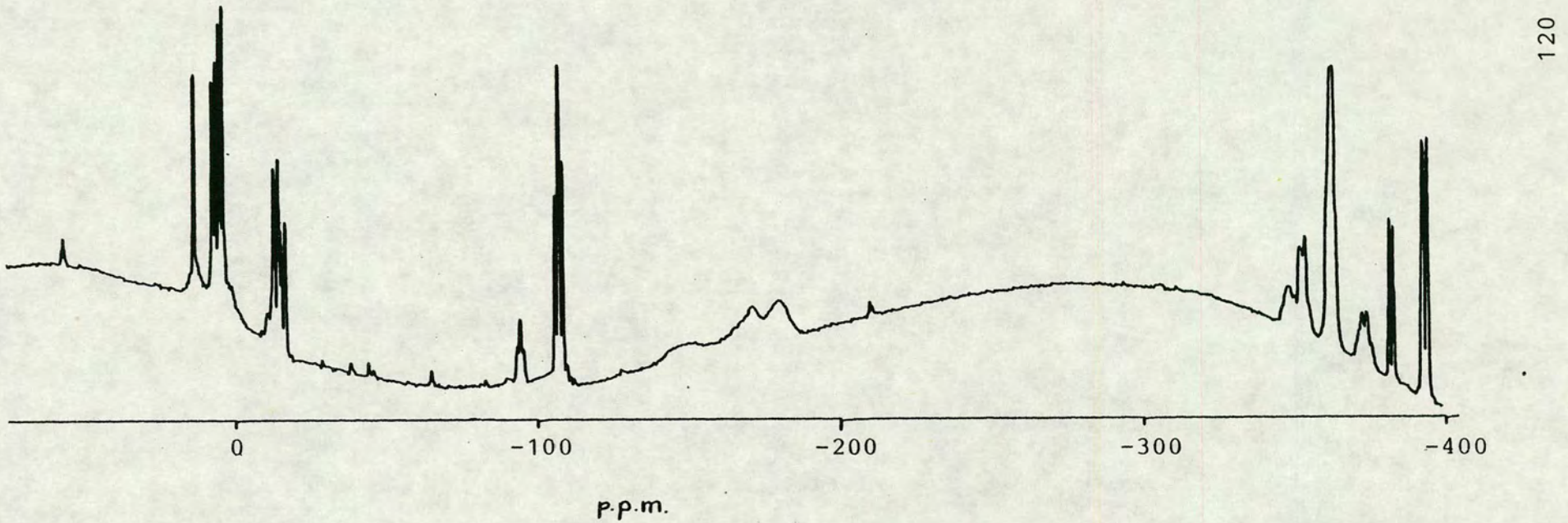


Table 4.3.2

Coupling Constants for Species [XXV]/Hz

Nuc.	F_{2A}	$F_{2A'}$	F_{2E}	F_{2M}
F_{2A}	-	177	85	n.o.
$F_{2A'}$	177	-	106	n.o.
F_{2E}	85	106	-	n.o.
F_{2M}	n.o.	n.o.	n.o.	-

On warming to 205K a very broad resonance had appeared in the region associated with CH_2ClF and HF. However, no change was observed in the resonances associated with complex [XXV]. On further warming to 210K there was a dramatic change in the spectrum, with all the Se-F and Rh-F resonances having disappeared and only resonances due to Et_3PF_2, CH_2ClF and HF being observed. On recooling to 195K from this temperature the resonances assigned to species were not reobserved, indicating that complete decomposition of complex [XXV], and indeed any other SeF_3 complex, had occurred at 210K.

The $^{31}P-\{^1H\}$ n.m.r. spectrum at 195K was, as had been observed in several of the previously discussed reactions, very unhelpful, showing merely a broad hump at around δ28. On observation at 210K the ^{31}P n.m.r. spectrum was extremely complicated and no useful information could be extracted from it.

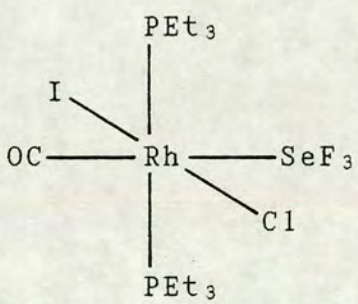
At 195K the $^{19}F-\{^1H\}$ n.m.r. spectrum also showed a weak triplet at δ-99.1 which showed signs of broadening on warming to 205K. Assuming that this is an equatorial Se-F resonance, no corresponding axial Se-F

resonances were observed in the expected region. This is not surprising as the intensity of the triplet was at approximately 10% of the intensity of the equatorial Se-F resonance of [XXV] and also, as we have observed on several occasions previously, it is likely that any axial Se-F resonances would not be visible due to imposition of far more intense resonances arising from more abundant species. No corresponding Rh-F resonance was observed in the expected regions.

No corresponding ^{31}P resonances were observed at either 81.015 or 145.785MHz, probably for the same reasons as were stated above.

The triplet form of the resonance at δ-99.1 at 195K shows that it must arise from a species more fluxional than [XXV]; since it is also to high frequency of the equatorial resonance of [XXV] we suggest that it arose from the equatorial Se-F resonance of a new complex, [XXVI];

[figure 4.3.3]



[XXVI]

However, the evidence for our assignment is very incomplete and therefore this is a very tentative proposal.

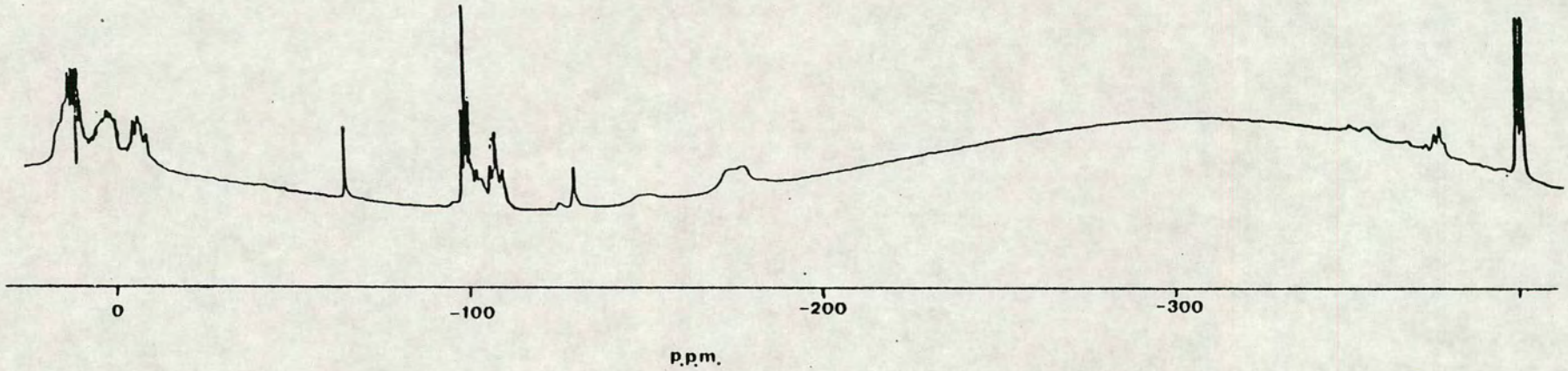
On warming to 210K this complex was also observed to have decomposed, indicating that the iodide SeF_3 complexes of rhodium are significantly less stable than their sulphur analogues.

4.4 Reaction of $Rh(CO)NCS(PEt_3)_2$ with SeF_4.

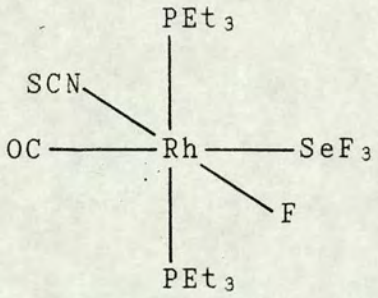
At 195K several resonances were observed in the $^{19}F-\{^1H\}$ n.m.r. spectrum [figure 4.4.1]. The most significant of these were four resonances, F_{3A}, $F_{3A'}$, F_{3E} and F_{3M} observed at δ12.5, δ-2.5, δ-99.3 and δ-401.0 respectively. The resonances observed in the Se-F regions of the spectrum lay in areas where other intense resonances appeared which resulted in poor resolution as we were unable to achieve a narrow enough spectral width from which to extract all of the couplings. As a result, the only coupling constants we were able to resolve from the Se-F resonances were the large, mutual F-F couplings. As the Rh-F resonance was in a relatively unobscured region of the spectrum we were able to resolve its couplings to Rh, two phosphine groups and a fluorine. The fact that we were able to observe a coupling to fluorine in the Rh-F resonance was fundamental in our assigning these four ^{19}F resonances as arising from an SeF_3 complex of rhodium, [XXVII].

As the chemical shifts of the Se-F resonances were observed at relatively high frequency and the Rh-F resonance was in the region of the spectrum associated with Rh-F *trans* to halide or pseudohalide, we have assigned complex [XXVII] as the isomeric form of the major products which we observed in the three previous reactions of SeF_4 discussed in this chapter;

Figure 4.4.1; $^{19}F-\{^{1}H\}$ n.m.r. Spectrum of $Rh(CO)NCS(PEt_3)_2$ + SeF_4 at 195K



[figure 4.4.2]

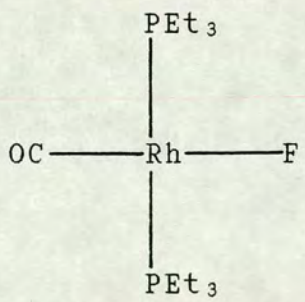


[XXVII]

The $^{31}P-\{^{1}H\}$ n.m.r. spectrum of this reaction was equally as unhelpful as that of the analogous iodide reaction, showing only a broad lump centred at approximately $\delta 27$.

On warming to 210K all traces of the four resonances in the $^{19}F-\{^{1}H\}$ n.m.r. had disappeared and did not reappear on cooling to 195K, indicating that complex [XXVII] had decomposed. We did observe very broad, intense resonances arising from the pentafluoroselenate(IV) anion, Et_3PF_2 and three Rh-F resonances at δ-264, δ-330 and δ-342. The resonance at δ-264 lay in the region associated with fluorine bonded to a Rh(I) nucleus and thus we have tentatively assigned this resonance as arising from the complex [XXVIII];

[figure 4.4.3]

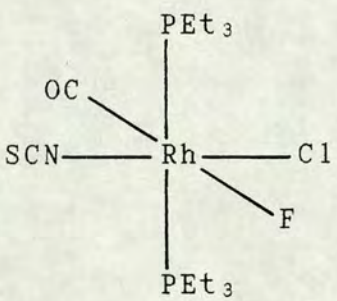


[XXVIII]

The ^{19}F n.m.r. spectrum of this complex has not been previously published but the complex has been characterised by our group using ^{31}P and ^{19}F n.m.r. spectroscopy. The ^{31}P n.m.r. spectrum of the decomposition products was so complicated that no information could be extracted from it.

The other two Rh-F resonances were observed in the region of the ^{19}F n.m.r. spectrum associated with fluorine bonded to Rh(III) and *trans* to CO. The resonance at δ-342 is within the resolution limit for the chemical shift of the fluoride of the *trans* dichloride complex, [VIII]. The other resonance at δ-330 is probably due to complex [XXIX];

[figure 4.4.4]

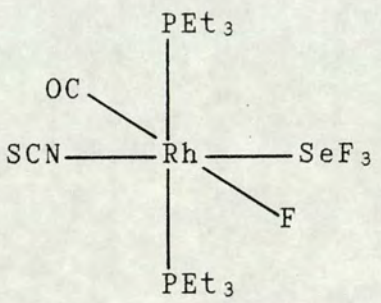


[XXIX]

Again this assignment is very tentative as we could not assign the ^{31}P resonance due to superposition of many resonances in the $^{31}P-\{^{1}H\}$ n.m.r. spectrum.

Also observed in the ^{19}F n.m.r. spectrum at 195K was an equatorial Se-F resonance at δ-106.6 and a Rh(III)-F resonance at δ-375. Both resonances were at the same intensity, approximately 40% of that of each resonance of [XXVII]. There was also evidence in the

axial Se-F region of the spectrum for axial Se-F resonances which may have been associated with these two resonances. On the basis of the chemical shifts of these resonances and by analogy with the previously discussed reactions we have very tentatively assigned these resonances as having arisen from complex [XXX]; [figure 4.4.5]



[XXX]

This complex was also observed to have decomposed at 210K.

The results of this reaction and the previously discussed iodide analogue shows us that the SeF_3 iodide and thiocyanate complexes, although formed, are extremely unstable when compared to the chloride and bromide analogues and the sulphur analogues.

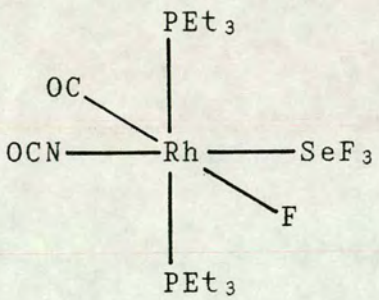
4.5 Reaction of $Rh(CO)NCO(PEt_3)_2$ with SeF_4

The $^{19}F-\{^1H\}$ n.m.r. spectrum observed at 195K was very similar to all of the previous spectra observed from the reaction of SeF_4 with $Rh(CO)X(PEt_3)_2$ [X = Cl, Br, I] [figure 4.5.2]. Four resonances of approximately equal intensities F_{4A}, $F_{4A'}$, F_{4E} and F_{4M} were observed; a doublet of doublets of doublets of doublets at δ6.1, a doublet of doublets of doublets of doublets of doublets at δ-11.4, a doublet of doublets of doublets of triplets at δ-103.4 and a doublets of triplets of doublets at δ-372.4. Parameters are detailed in tables 4.5.1 and 4.5.2.

The $^{31}P-\{^1H\}$ n.m.r. spectrum at 195K showed a broad and unresolved AB pattern whose chemical shifts were in the region of the spectrum associated with PR_3 bonded to Rh(III).

On the basis of these chemical shifts and the coupling constants we have assigned these spectra as arising from complex [XXXI];

[figure 4.5.1]



[XXXI]

Figure 4.5.2; $^{19}F-\{^{1}H\}$ n.m.r. Spectrum of $Rh(CO)NCO(PEt_3)_2$ + SeF_4 at 195K

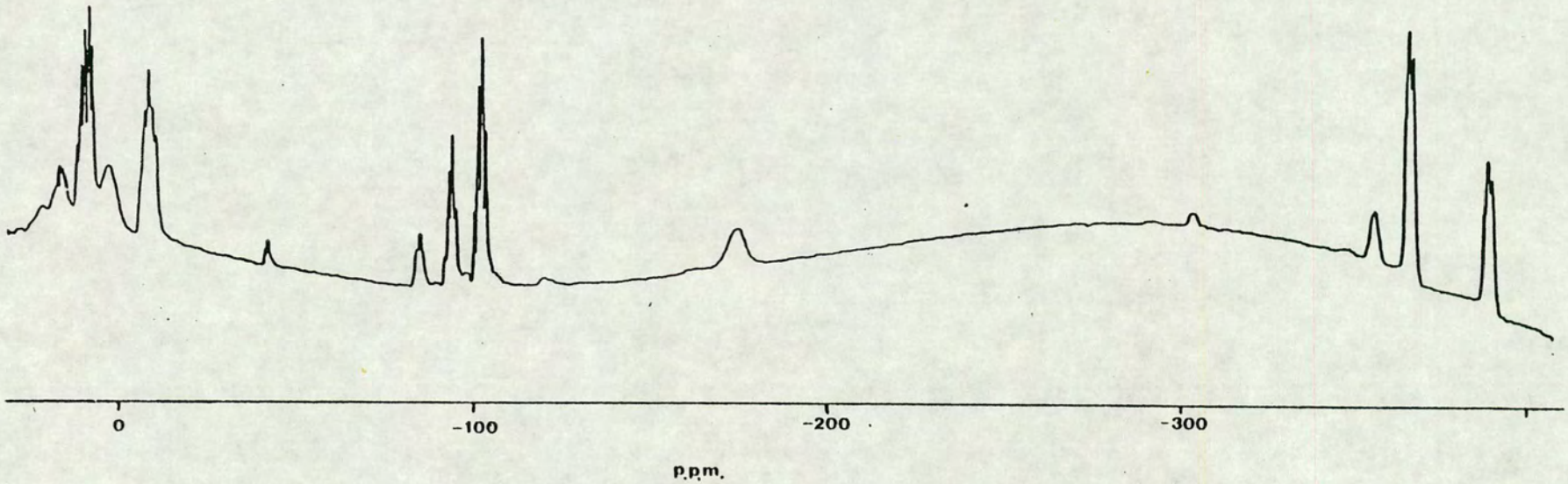


Table 4.5.1

Chemical Shifts for Species [XXXI]/p.p.m.

Se-F			Rh-F	P	
F_{4A}	$F_{4A'}$	F_{4E}	F_{4M}	P_A	P_B
6.1	-11.4	-103.4	-372.4	40	29

TABLE 4.5.2

Coupling Constants for Species [XXXI]/Hz

Nuc.	F_{4A}	$F_{4A'}$	F_{4E}	F_{4M}	P	Rh
F_{4A}	-	172	87	n.o.	6	16
$F_{4A'}$	172	-	103	10	20	20
F_{4E}	87	103	-	n.o.	6	14
F_{4M}	n.o.	10	n.o.	-	26	119
P	6	20	6	26	-	n.o.

On warming to 215K the axial Se-F resonances had lost all of their couplings and the Rh-F resonance showed only its coupling to rhodium. At 220K the axial Se-F resonance had begun to broaden, the equatorial Se-F resonance had now become a triplet and the Rh-F resonance was still poorly resolved. At 225K the axial Se-F resonances were broader still, the equatorial Se-F resonance was still a sharp triplet and now, the Rh-F resonance began to sharpen up. At 255K the axial Se-F resonance was no longer visible and a new resonance was observed at δ-0.8. This was a doublet of triplets of doublets [F_{AX} figure 4.5.3]. At this temperature the resonance at δ-103.4 was observed to have moved to lower frequency to δ-106.4 and had resolved to a triplet of doublets of triplets [figure 4.5.4]. As the new

Figure 4.5.3; Expansion of F_{AX}

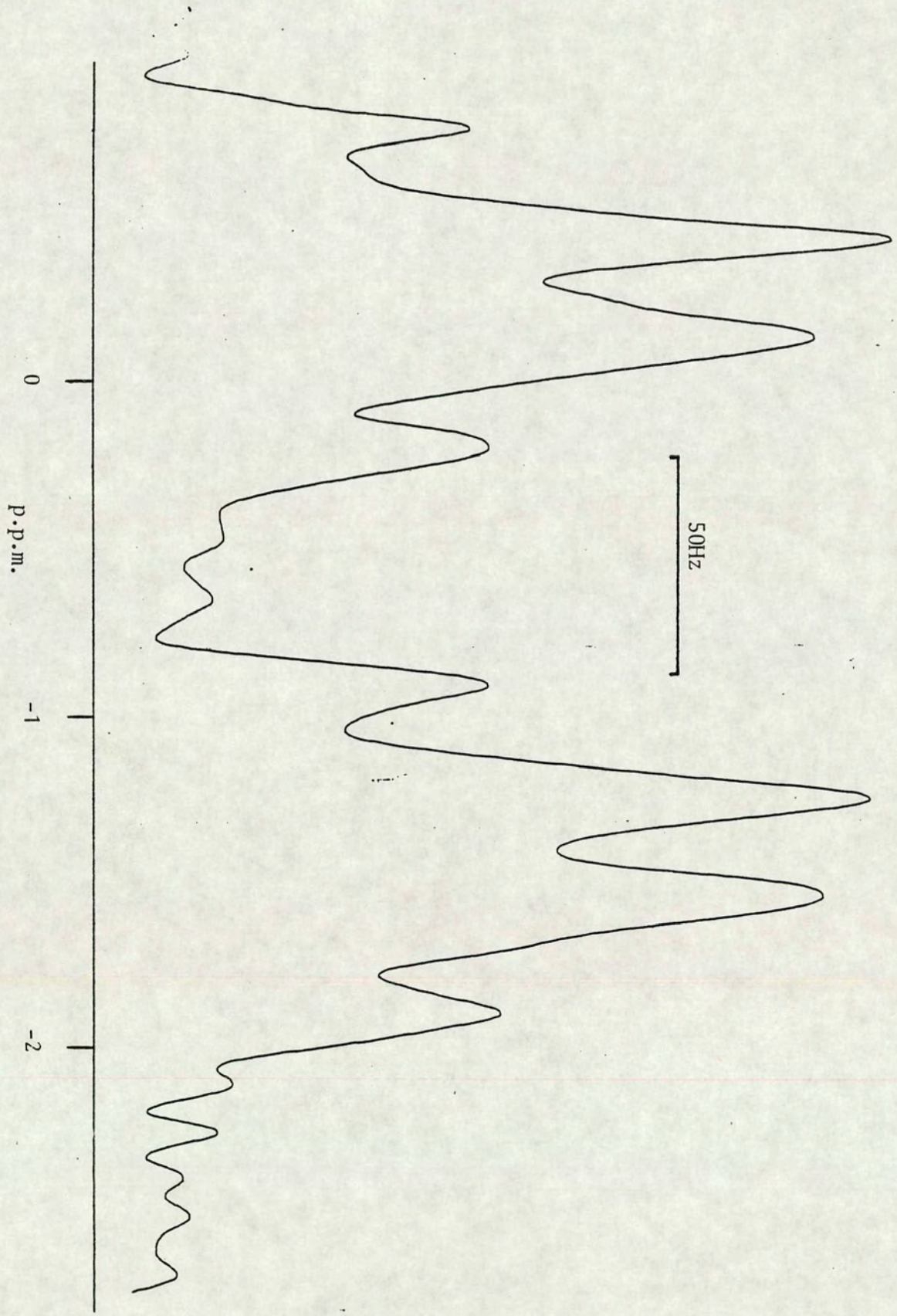


Figure 4.5.4; Expansion of F_{EQ}

resonance at δ-0.8 was at approximately twice the intensity of the resonance at δ-372.4, which had now resolved into a doublet of triplets of triplets, we assumed that it was the coalesced axial Se-F resonance arising as a result of a fluxional process which had caused the axial Se-F's to become equivalent.

In an attempt to confirm that these three resonances arose from the same complex we decided to perform a 2-dimensional n.m.r. experiment.

A ^{19}F-^{19}F COSY[44] n.m.r. spectrum was run of the solution at 255K [figure 4.5.5]. The presence of cross peaks between the resonances at δ-0.8 and δ-106.4 proved that these two resonances did indeed couple to each other and therefore must arise from the same complex, and since we also observed a mutual coupling between the resonances at δ-372.4 and δ-106.4 we can be certain that the n.m.r. spectra observed result from complex [XXXI] in which the axial Se-F's are equivalent due to a rocking or rotation about the Rh-Se bond which is fast on the n.m.r. timescale. Parameters obtained from these resonances are detailed in tables 4.5.3 and 4.5.4.

The ^{31}P-$\{^{1}H\}$ n.m.r. spectrum at 195K was relatively well-resolved, showing an overlapping pair of doublets, the more intense of which we have assigned as arising from the two equivalent PEt_3 groups bonded to complex [XXXI] due to resolution of $^{2}J_{P-FM}$.

Figure 4.5.5; ^{19}F-^{19}F COSY n.m.r. Spectrum of $Rh(CO)NCO(PEt_3)_2$ + SeF_4 at 195K

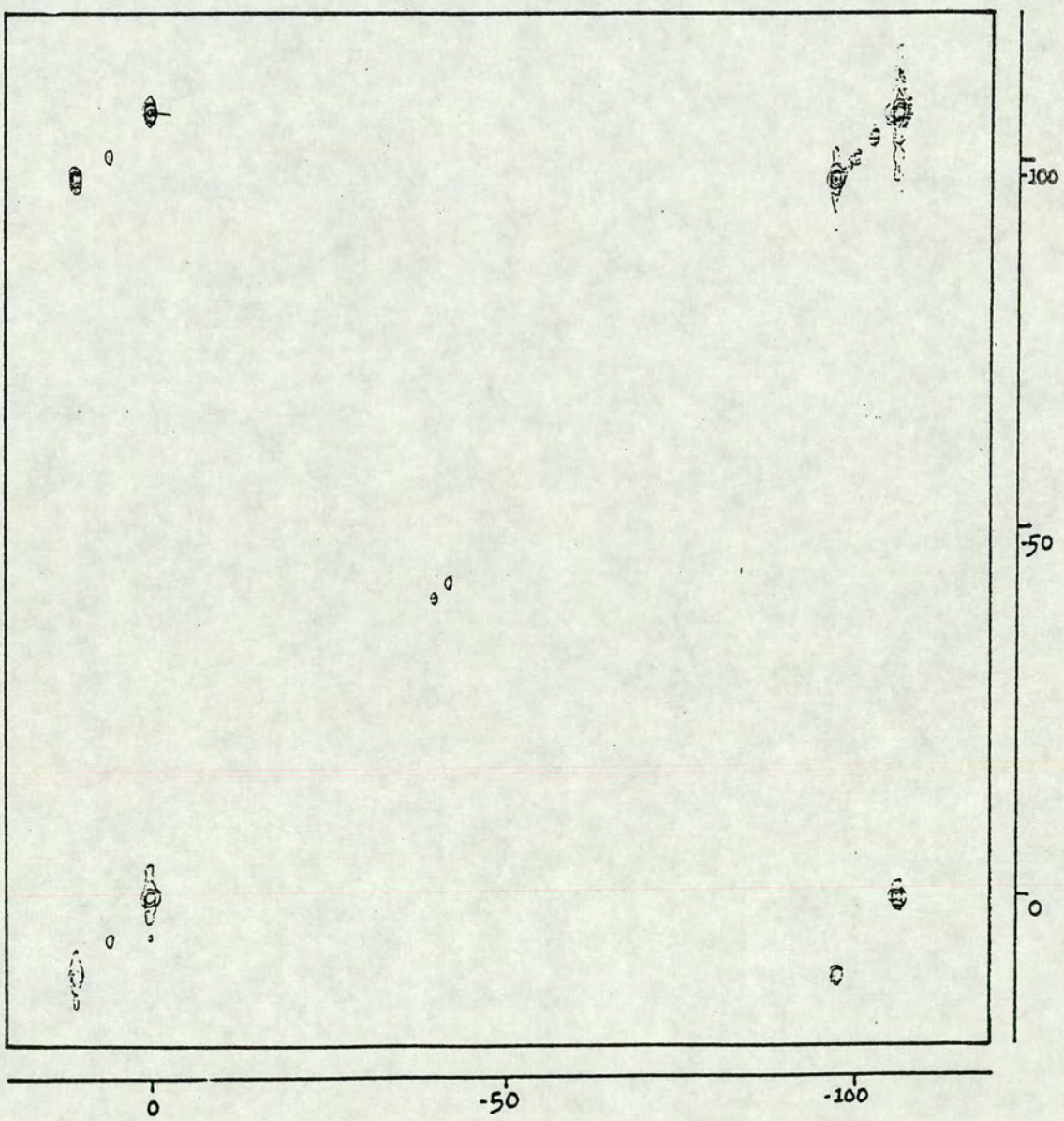


Table 4.5.3

Chemical Shifts for Species [XXXI] at 255K/p.p.m.

Se-F		Rh-F	P
F_{4AX}	F_{4E}	F_{4M}	P
-0.8	-106.4	-372.4	34.3

Table 4.5.4

Coupling constants for species [XXXI] at 255K/Hz

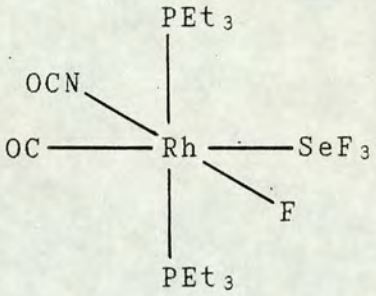
Nuc.	F_{4AX}	F_{4E}	F_{4M}	P	Rh
F_{4AX}	-	97	19	15	19
F_{4E}	97	-	n.o.	7	14
F_{4M}	19	n.o.	-	10	118
P	15	7	10	-	68

On recooling from this temperature to 195K the original four resonances were again observed in the $^{19}F-\{^{1}H\}$ n.m.r. spectrum, indicating that the fluxional process was completely reversible. On warming further, no change was observed until 300K when decomposition was observed to have occurred. Only resonances due to Et_3PF_2, HF and CH_2ClF were observed.

Also observed at 195K were four resonances of approximately equal inensities f_{4A}, $f_{4A'}$, f_{4E} and f_{4M} at δ16.9, δ3.6, δ-94.9 and δ-390.7 respectively which were at approximately 40% of the intensity of each resonance of [XXXI]. The $^{31}P-\{^{1}H\}$ n.m.r. spectrum at 195K showed a broad, unresolved resonance at δ34.1, the region associated with PR_3 bonded to Rh(III). On the basis of these chemical shifts and the ratio of their integrals to those of complex [XXXI] we have assigned these n.m.r.

data as arising from complex [XXXII];

[figure 4.5.6]



[XXXII]

The two axial Se-F resonances were both rather broad and unresolved and the Rh-F resonance merely showed coupling to rhodium, whilst the equatorial Se-F resonance was a sharp triplet. The most likely explanation for the axial Se-F resonance being broad is that the two axial Se-F's are beginning to undergo fluxional behaviour. This is consistent with our previous results, as complexes in which CO is *trans* to MF_3 [M = S, Se] were observed to be more fluxional than their isomers where halide or pseudohalide is *trans* to MF_3.

On warming to 210K, all four resonances were observed to have broadened and lost their couplings. At 215K the axial Se-F resonances were no longer visible. Either they had broadened and become indistinguishable from the baseline or else they had become obscured by the intense axial Se-F resonances of [XXXI]. At 240K a sharp resonance had appeared at δ9.7. This appeared to be a doublet. Since this resonance was at twice the intensity of the, still visible, equatorial Se-F and Rh-

F resonances and the axial Se-F resonances were still not visible, we have assigned this new resonance as arising from two equivalent axial Se-F nuclei. At 255K this axial Se-F resonance had resolved into a sharp doublet of triplets of doublets. The equatorial Se-F resonance was a sharp triplet of doublets of triplets at this temperature but the Rh-F resonance remained broad and unresolved.

These observations suggested that the SeF_3 group was undergoing an intramolecular exchange process which was fast on the n.m.r. timescale and simultaneously the Rh-F was undergoing a different exchange which was also fast on the n.m.r. timescale. Little can be deduced about the nature of the Rh-F exchange from the information we have. However, we believe that the exchange is likely to be intermolecular as we do not observe any effects that intramolecular exchange would have on the chemical shifts of the SeF_3 group. Thus we believe it is likely that the Rh-F is exchanging with HF as we also observe a characteristic broad HF resonance in the $^{19}F-\{^1H\}$ n.m.r. spectrum but no SeF_5^-.

We previously assigned the most intense doublet of a pair of overlapping doublets in the $^{31}P-\{^1H\}$ n.m.r. spectrum as arising from complex [XXXI], similarly, on the basis of its chemical shift and integral, we have assigned the less intense doublet as arising from the two equivalent PEt_3 groups of [XXXII].

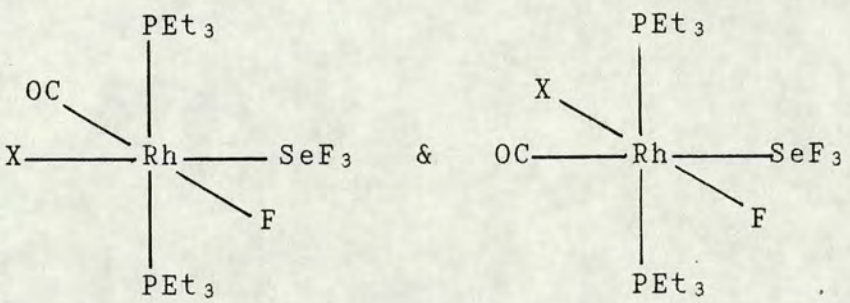
On further warming no change was observed in the ^{19}F or ^{31}P n.m.r. spectra until decomposition was observed at 290K.

4.6 Discussion

The work in this chapter has shown that rhodium complexes of the form $Rh(CO)X(PEt_3)_2$ [X = Cl, Br, I, NCS and NCO] oxidatively insert the rhodium into an Se-F bond of SeF_4. This behaviour is analogous to the result in the analogous reactions with SF_4.

We have also observed that two isomeric Rh-SeF_3 complexes are formed on reaction of SeF_4 with each rhodium complex;

[figure 4.6.1]



[I] [II]

On comparison of the ratio [I] : [II] for the complexes where X = halide we observe that as the bulk of X increases, the ratio increases. This result is consistent with our observations and explanation of the ratios of complexes in the analogous sulphur systems discussed in section 3.5.

In the isothiocyanate reaction we see more of [II] than [I]. This is not surprising as the NCS ligand is bonded to the rhodium via the small N-donor end. However, we would expect, as we did observe in the analogous sulphur systems, that the ratio [I] : [II] should be smaller in the NCO reaction than in the NCS

reaction as, overall, the NCS ligand is bulkier than NCO but we observe the reverse. This is possibly a result of the bulky part of the ligand being further from rhodium in the isothiocyanate complex than in the isocyanate complex. Comparison of the x-ray crystal structures of $Ti(\eta^5\ Cp)_2(NCS)_2$[73] and $Ti(\eta^5\ Cp)_2(NCO)_2$[74] shows that in the isothiocyanate complex the sulphur is 4.8Å from rhodium and in the isocyanate complex the oxygen is 4.4Å away.

The fluxionalities of the SeF_3 groups in these complexes vary in a similar manner to the analogous sulphur complexes. We cannot discuss the fluxionalities of the iodide or isothiocyanate complexes as they had decomposed before any fluxional behaviour was observed. We observed that type [I] complexes became less fluxional as X was varied from NCO -> Cl -> Br which is identical to what was observed in the analogous sulphur systems.

Since no type [II] complex was observed in the bromide reaction we can only compare the type [II] complexes of chloride and isocyanate and so we observe that, again, as in the analogous sulphur systems the fluxionality of the SeF_3 group increases as X changes from NCO -> Cl.

Comparing the fluxionalities of the MF_3 groups in analogous sulphur and selenium systems shows that the selenium systems become fluxional at lower temperatures than their sulphur analogues. The reason for this difference is more likely to be electronic than steric

as the empty dπ orbitals on Se will have less overlap with the filled dπ orbitals of rhodium than those of sulphur will, making rotation easier.

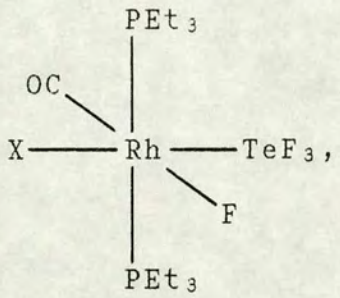
We have also observed that, although rotation about the rhodium-sulphur bond is easier in Rh-SeF_3 complexes than in the analogous SF_3 complexes, Berry-pseudorotation is not observed at selenium. We believe that this is possibly a consequence of the longer Rh-Se bond and longer Se-F bonds which could lead to a "locking-in" of the longer axial fluorines by the ethyl groups of the phosphine ligand by steric interactions. This may enable the SeF_3 group to undergo full rotation but not pseudorotation.

We have also observed that, unlike the analogous sulphur systems, the Rh-F undergoes intermolecular exchange in some of the complexes. This means that the Rh-F bond must be more reactive in these systems. It is known that transition metal-fluoride bonds are not particularly stable in coordination compounds. This is illustrated by the fact that there are very few examples of complexes containing an M-F bond. However, these bonds are stabilised by high oxidation state metals e.g. $Rh(VI)F_6$ and $Ir(VI)F_6$. This stabilisation is probably due to the fact the fluoride ligands can donate p-electrons into the empty metal d-orbitals and so stabilise the M-F bond. It may be that as we exchange S for Se in our systems we will reduce the amount of electron withdrawal from rhodium making

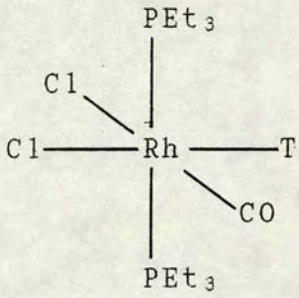
the rhodium less likely to accept p-electrons from the fluoride ligand and thus make exchange of fluoride more facile. A second possible explanation for the increased reactivity in Rh-SeF_3 complexes compared with Rh-SF_3 complexes is that the alkyl groups of the PEt_3 ligands are pushed further away from the Rh-F in SeF_3 complexes than in SF_3 complexes due to increased steric interaction with the selenium-fluoride nuclei as a result of longer Se-F bonds. We know that the complexes $Rh(CO)F(PR_3)_2$ [R = Et, Me] are unknown but when R = Ph or Cy the complexes are well known and stable due to stabilisation of the reactive Rh-F bond by the bulky phosphine groups. This explanation is very tentative as are all the explanations we have suggested to account for the fluxional behaviour of these complexes. A series of crystal structures would help to solve the questions raised by the fluxionalities as we could then compare, physically, the bond lengths and steric crowding from one complex to the other.

Chapter Five.

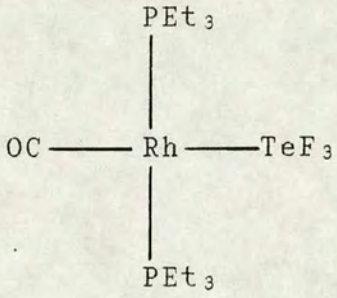
Key to Structures and Numbers in Chapter 5.



[XXXIII]



[XXXIV]



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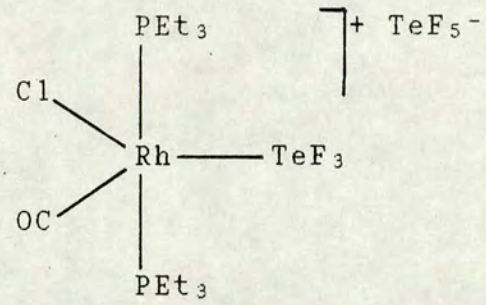
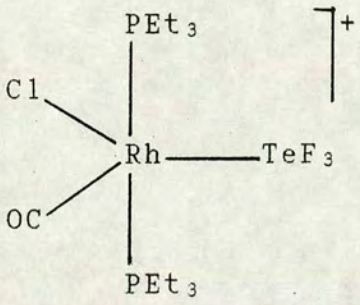
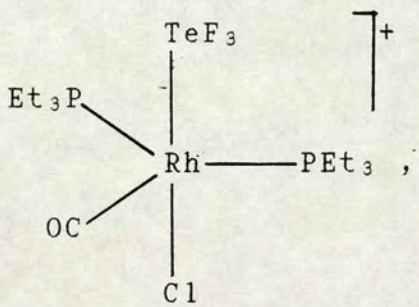


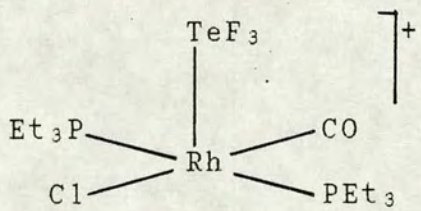
[XXXVI]



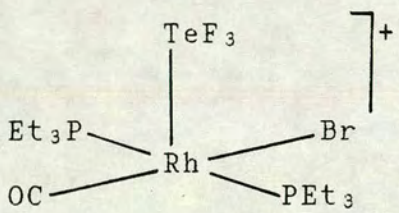
[XXXVII]



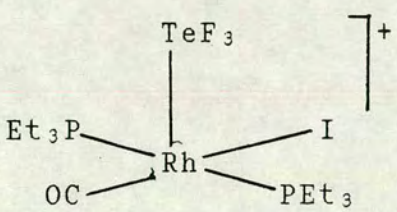
[XXXVIII]



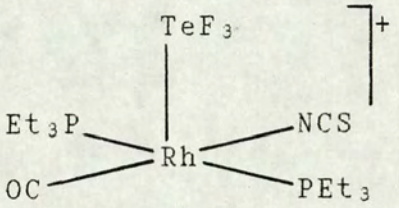
[XXXIX]



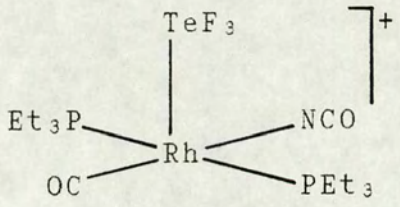
[XL]



[XLI]



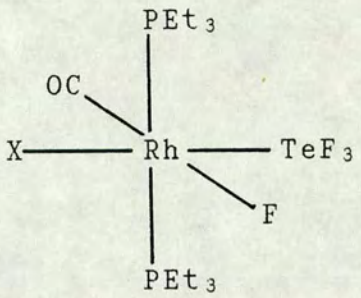
[XLII]



[XLIII]

Reactions of TeF_4.

Since SF_4 and SeF_4 were both observed to react with rhodium(I) phosphine complexes to give the oxidative addition products containing SF_3 or SeF_3 ligands, we decided to investigate the reaction of TeF_4 with complexes of the form $Rh(CO)X(PEt_3)_2$ [X = Cl, Br, I, SCN, OCN] in an attempt to form products of the type; [figure 5.1]



[XXXIII]

5.1 Reaction of $Rh(CO)Cl(PEt_3)_2$ with TeF_4.

As in all the previously discussed reactions, this was observed by $^{19}F-\{^1H\}$ n.m.r. spectroscopy at 195K. On melting, the solution became deep red and a spectrum was obtained which was simpler than those seen previously in any of the reactions between sulphur and selenium tetrafluoride with rhodium complexes. Four resonances, F_1, F_2, F_3 and F_4 were observed whose ratios were approximately 2:1:4:1 respectively [figure 5.1.1]. These were a doublet of doublets of triplets at δ-9.6, an asymmetric quintet at δ-30.9, a doublet at δ-41.9 and a resonance at δ-68.4 which was, for some reason, difficult to resolve. In this resonance we could easily pick out a large triplet and, with difficulty, a smaller doublet. There was evidence for further splitting but we could not extract any further information. Each of the four resonances had satellites indicating 1-bond coupling to ^{125}Te and, indeed, the doublet was strong enough to enable us to observe coupling to the low abundance ^{123}Te nucleus. Expansions of all four resonances are given in figures 5.1.2 and 5.1.3. The two resonances at δ-30.9 and δ-41.9 were identified as arising from the axial and equatorial F nuclei of the pentafluorotellurate(IV) ion, TeF_5^- ($^2J_{F-F}$ = 56Hz)[72]; [figure 5.1.1]

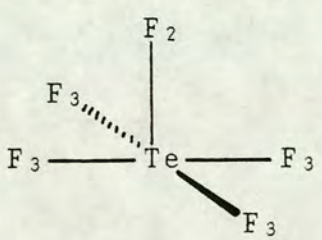


Figure 5.1.2; $^{19}F-\{^{1}H\}$ n.m.r. spectrum of $Rh(CO)Cl(PEt_3)_2$ + TeF_4

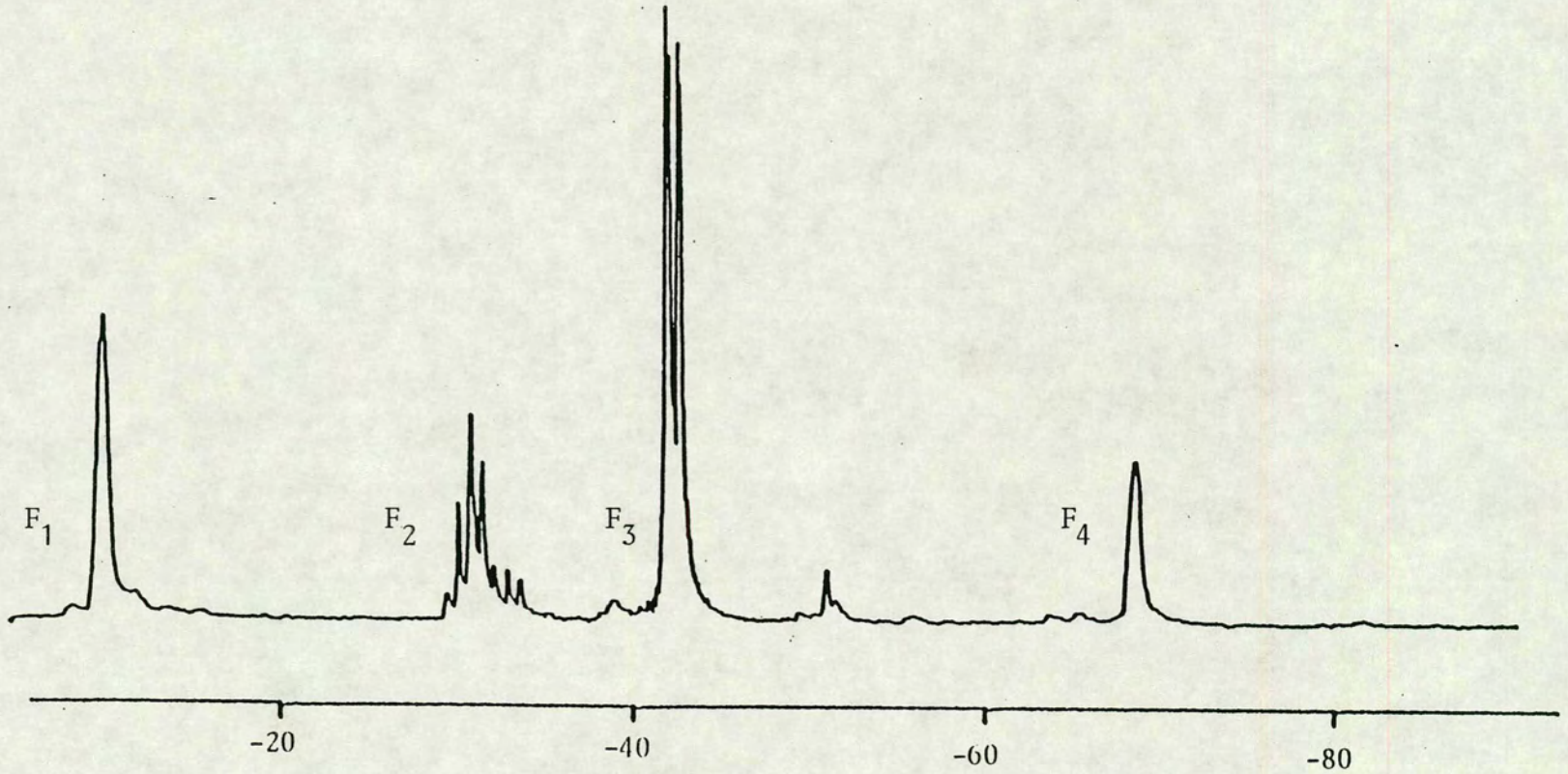


Figure 5.1.3; Expansions of F_1 & F_2

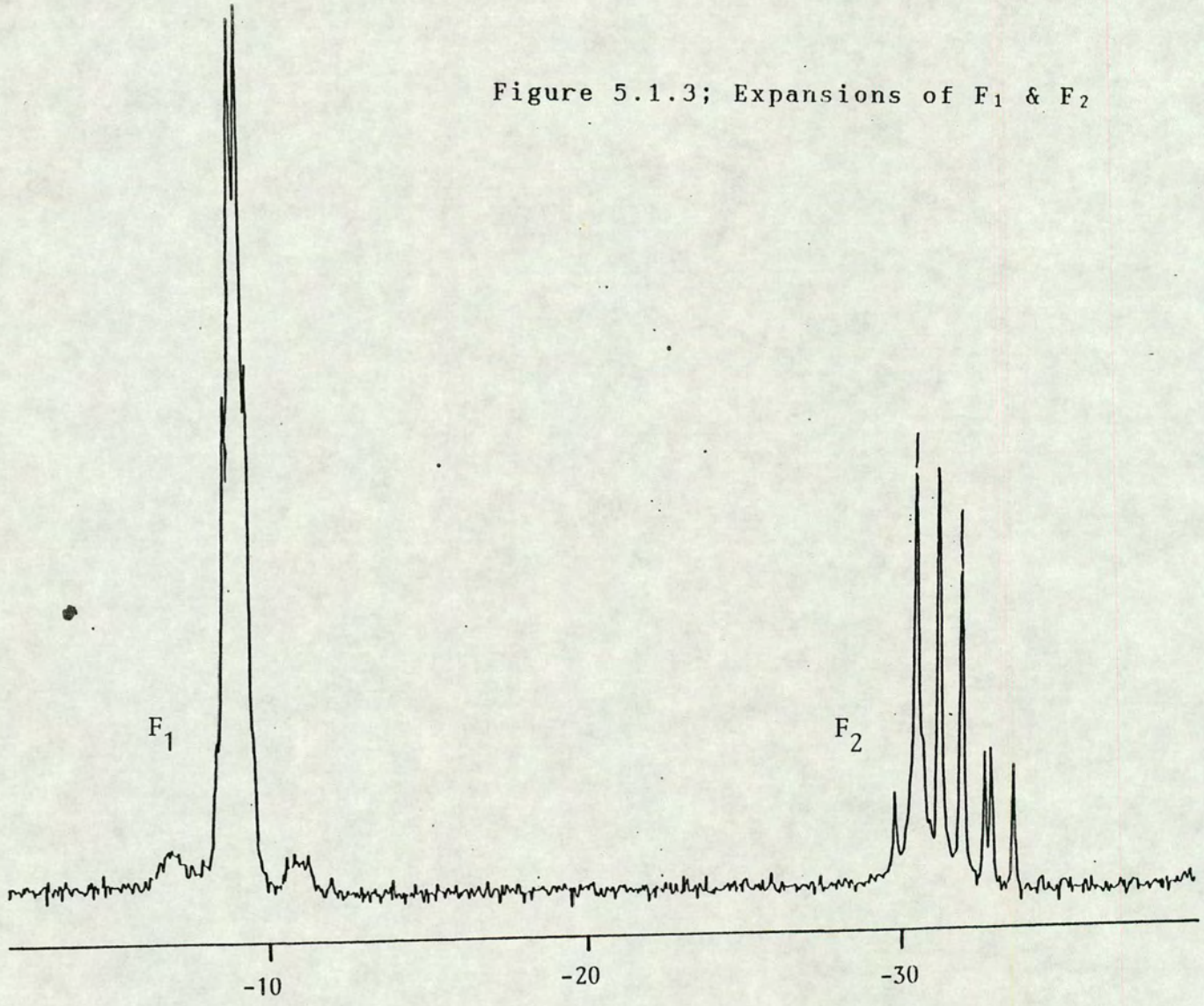
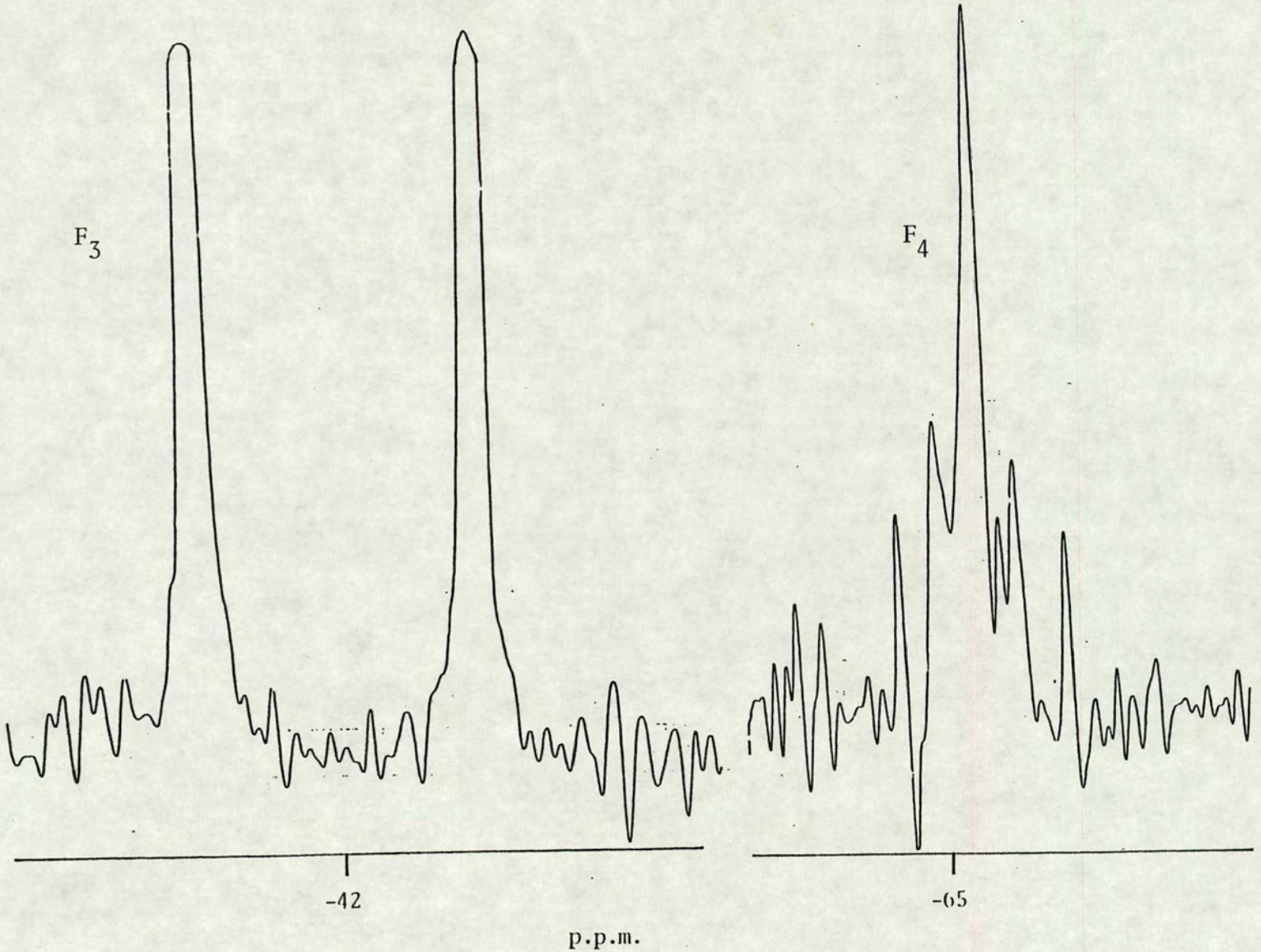


Figure 5.1.4; Expansions of F_3 & F_4

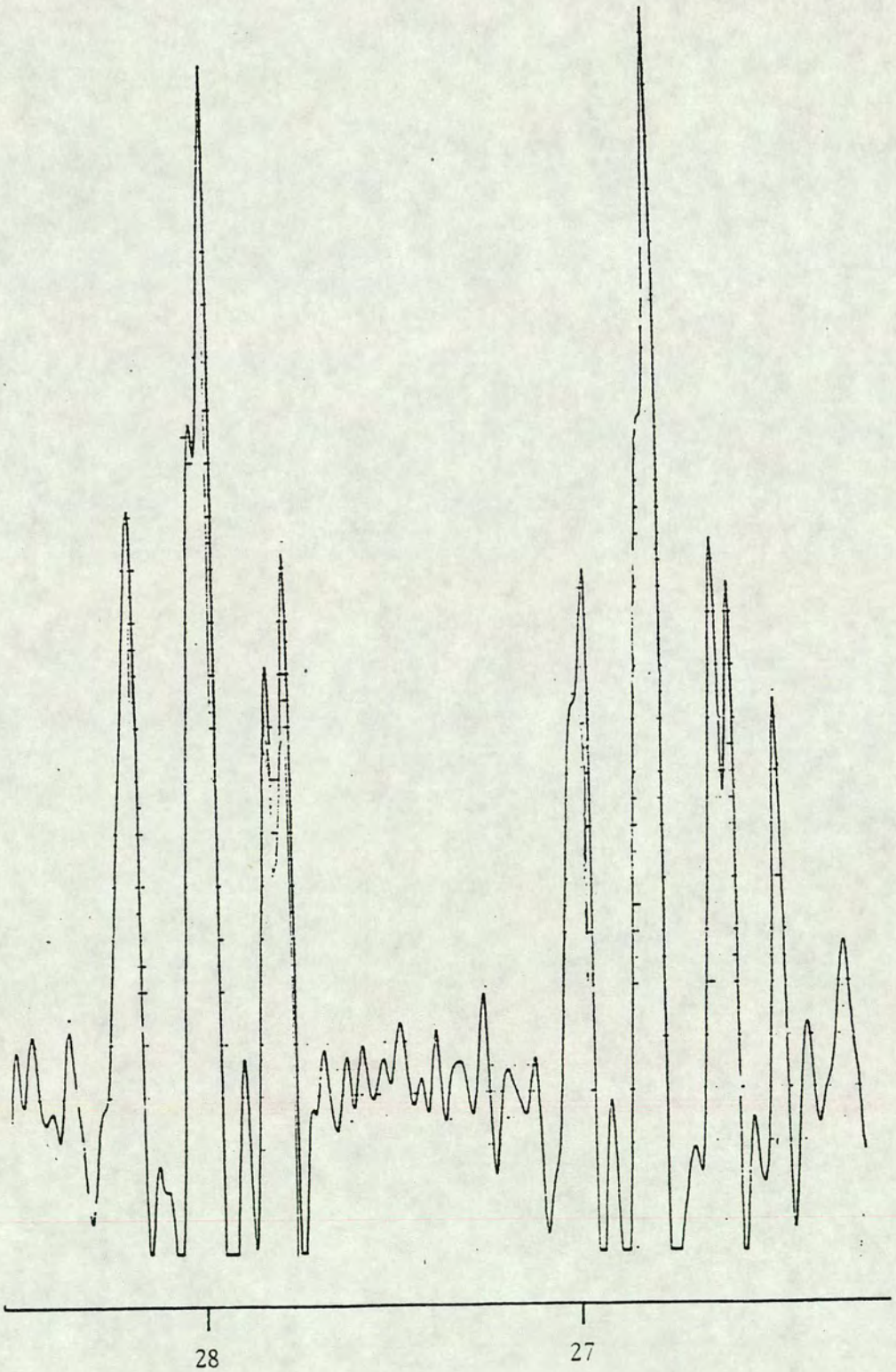


This result was not surprising as we had seen resonances due to SeF_5^- ions in some of the reactions of SeF_4.

The reason that the quintet at δ-30.9 was asymmetric was due to second order effects. Since the operating frequency of the spectrometer was 75.39MHz, the difference in the chemical shifts of the two ^{19}F resonances of TeF_5^- was 829Hz and $^2J_{F-F}$ was 56Hz. If $\delta A - \delta B \sim 15J_{A-B}$ then a second order effect is observed[46]; the spectrum at 188.475MHz showed a symmetrical, first order quintet.

We felt unable to assign either of the remaining two resonances without observing the $^{31}P-\{^1H\}$ n.m.r. spectrum. At 195K this showed two resonances of approximately 1:1 ratio, a doublet of triplets of narrow doublets at δ27.4 and a doublet at δ24.3 which was due to unreacted $Rh(CO)Cl(PEt_3)_2$ [figure 5.1.5]. In the resonance at δ27.4 the triplet coupling of 16Hz was equivalent to the triplet coupling observed in the ^{19}F resonance at δ-9.6, indicating that two equivalent phosphorus nuclei may be coupling to two equivalent fluorine nuclei. The magnitude of the coupling also suggested that this was a 3-bond $^3J_{P-F}$. The large doublet coupling of 92Hz was of the correct order for $^1J_{P-Rh}$. However it was rather large for $^1J_{(Rh-P)}$ between a PEt_3 group coupling to 6 coordinate Rh(III), which is normally of the order 65-80 Hz[50] and yet was small for $^1J_{P-Rh}$ between PEt_3 and a 4 coordinate Rh(I), which is normally of the order 115-120Hz[50]. The significance of

Figure 5.1.5; $^{31}P-\{^{1}H\}$ n.m.r. spectrum of $Rh(CO)Cl(PEt_3)_2$ + TeF_4

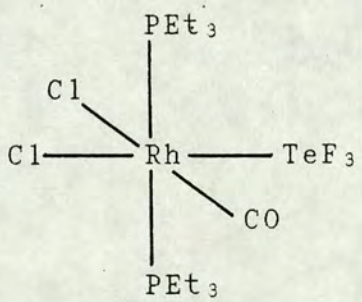


this will be discussed later in this chapter. The small doublet coupling of 3Hz was consistent with $^{3}J_{P-F}$, but as we could not resolve the ^{19}F resonance at δ-68.4 we could not assign this coupling.

The evidence of both the ^{19}F and the ^{31}P n.m.r. spectra was consistent with the presence of a TeF_3 group bonded directly to a Rh atom which was also bonded to two phosphine groups. If this is the case then there are three types of products which would fit the data observed.

The first is a complex of 6 coordinate Rh(III) of the type observed in the analogous reactions of SF_4 and SeF_4;

[figure 5.1.6]



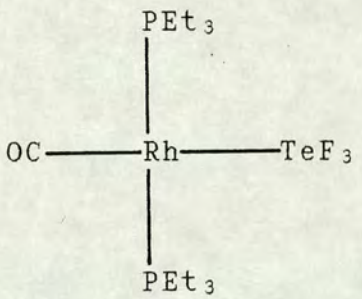
[XXXIV]

We feel that this is unlikely as there is no indication of fluorinated solvent, the formation of which normally accompanies chlorination of the complex in the analogous sulphur and selenium systems, neither is there evidence in the $^{31}P-\{^{1}H\}$ n.m.r. spectrum for decomposed $Rh(CO)Cl(PEt_3)_2$ which could also be a source of the second chloride.

The second possibility is a four coordinate

Rh(I) complex of the form;

[figure 5.1.7]

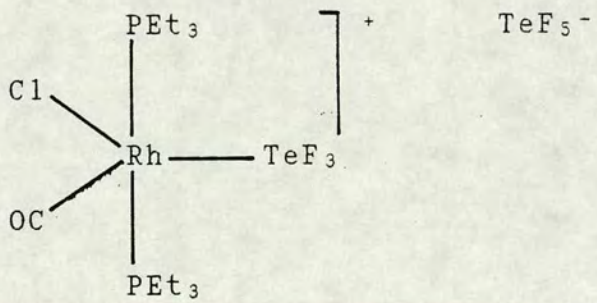


[XXXV]

This also seems unlikely, as the $^{1}J_{P-Rh}$ coupling constant observed is too small to be due to a square planar complex of this form, and there appears to be no obvious chlorinated product which would have arisen from the loss of chloride from $Rh(CO)Cl(PEt_3)_2$.

The third possibility is a 5 coordinate Rh(III) cationic species with the TeF_5^- as counterion;

[figure 5.1.8]



[XXXVI]

This structure is one possible geometry which is consistent with all of our n.m.r. data. Also there was no evidence for any other counterion for the TeF_5^- e.g. H^+ or $HPEt_3^+$. On repeating the reaction with a ratio of 2:1 TeF_4 to $Rh(CO)Cl(PEt_3)_2$ no starting

material was observed in the $^{31}P-\{^{1}H\}$ n.m.r. spectrum which is consistent with this assignment. Hereafter a 2:1 ratio of Te:Rh was used.

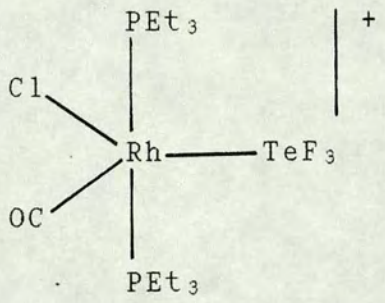
We shall now reconsider the significance of the magnitude of $^{1}J_{P-Rh}$.

In a 6 coordinate Rh(III) complex the normal magnitude of this coupling is 65-80Hz[50] compared to 110-120Hz in 4 coordinate Rh(I)complexes[50]. One simple explanation for these differences is that in the Rh(III) complex all six metal-ligand bonds can be considered as d^2sp^3 hybrids so each bond has 1/6 s character but in the square planar Rh(I) complexes all four metal-ligand bonds will be dsp^2 hybrids meaning that each bond has 1/4 s character. Since the magnitude of a 1-bond coupling constant depends on the amount of s character in that bond we would thus expect $^{1}J_{P-Rh}$ to be greater in the 4 coordinate complex than in the six coordinate example, which is indeed what one observes.

If we now apply this argument to 5 coordinate complexes, we have three possibilities. If both phosphine groups are equivalent then the complex must be either;

i) trigonal bipyramidal with both PEt_3 ligands axial;

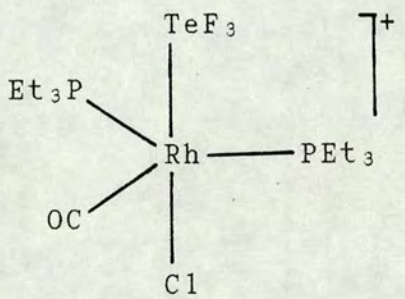
[figure 5.1.9]



[XXXVII]

ii) trigonal bipyramidal with both PEt_3 ligands equatorial;

[figure 5.1.10]

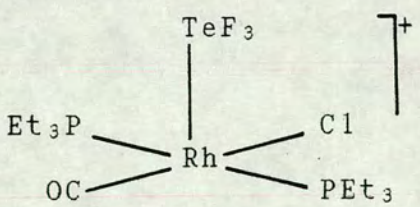


[XXXVIII]

or

iii) square pyramidal with both PEt_3 ligands lying *trans* in the square plane;

[figure 5.1.11]



[XXXIX]

In the first two cases the hybridisation is dsp^3 but the axial bonds will be dp hybrids having no s character and thus smaller coupling than in the 4 and 6

coordinate examples and the equatorial bonds will be sp^2 hybrids having more s character and thus larger coupling than in either the square planar or the octahedral cases. If it is iii) then the complex has C_{4v} symmetry meaning that the hybrid orbitals will have very complicated symmetry making the hybridisation arguments which we have used above too simplistic in this case.

Surprisingly, few examples of $^1J_{P-Rh}$ are quoted in the literature for 5 coordinate Rh(III) complexes of this type. However, the examples which are there quote a value of between 112 and 120Hz for $^1J_{P-Rh}$ in trigonal bipyramidal complexes having the phosphines in the equatorial plane, and a value of 90-98Hz for square pyramidal complexes with both phosphines in the equatorial plane[75,76]. This suggests that the 92Hz $^1J_{P-Rh}$ does not arise from either a 6 coordinate Rh(III) complex or a 4 coordinate Rh(I) complex, but is most likely due to a square based pyramidal complex [XXXIX] in which we possibly have ion pair formation, with one of the fluorines from the TeF_5^- ion weakly coordinating to the vacant coordination site on the rhodium. If this is the case then this coordination must be extremely weak as no coupling to rhodium is observed in the ^{19}F resonances of the TeF_5^- ion.

One major problem with this assignment is that we were unable to observe a mutual coupling between F_1 and F_4. F_1 did show a doublet coupling of 19Hz and F_4 a triplet coupling of 23Hz but the difference between

these is well above the resolution of the n.m.r. spectra observed. Also, if F_1 and F_4 arose from the axial and equatorial fluorines of a TeF_3 group we would have expected a much larger coupling between them, as seen in the analogous sulphur and selenium systems.

In an attempt to resolve this problem, two different n.m.r. experiments were performed. The first was a $^{19}F-\{^{19}F\}$ experiment. This was carried out at 188.305MHz and the resonance at δ-68.4 was irradiated. The resulting n.m.r. spectrum showed a definite, although slight, change in the resonance at δ-9.6 but no change in either of the other two resonances [figure 5.1.12]. We therefore decided to perform a second experiment. A $^{19}F-^{19}F$ COSY n.m.r. spectrum was run at 282.713MHz. The resulting spectrum [figure 5.1.13] showed cross peaks, as expected, between the two TeF_5- resonances, as well as cross peaks between F_1 and F_4 confirming that the two resonances at δ-9.6 and δ-68.4 are, indeed, coupled to each other.

A sample of the starting material enriched with 50% ^{13}C in the carbonyl group $[Rh(^{13}CO)Cl(PEt_3)_2]$ was prepared and allowed to react with TeF_4 in an attempt go gain further information on this species by observation of its ^{13} C n.m.r. spectrum.

At 195K the ^{13}C n.m.r. spectrum showed a doublet of triplets of doublets at δ180.9 [figure 5.1.14] which was consistent with a carbonyl group bonded to one rhodium ($^1J_{C-Rh}$ = 72Hz), two phosphines ($^2J_{C-P}$ = 11Hz) and one fluorine ($^3J_{C-F}$ = 8Hz). As the

Figure 5.1.12; $^{19}F-\{^{19}F\}$ n.m.r. spectrum of $Rh(CO)Cl(PEt_3)_2 + TeF_4$

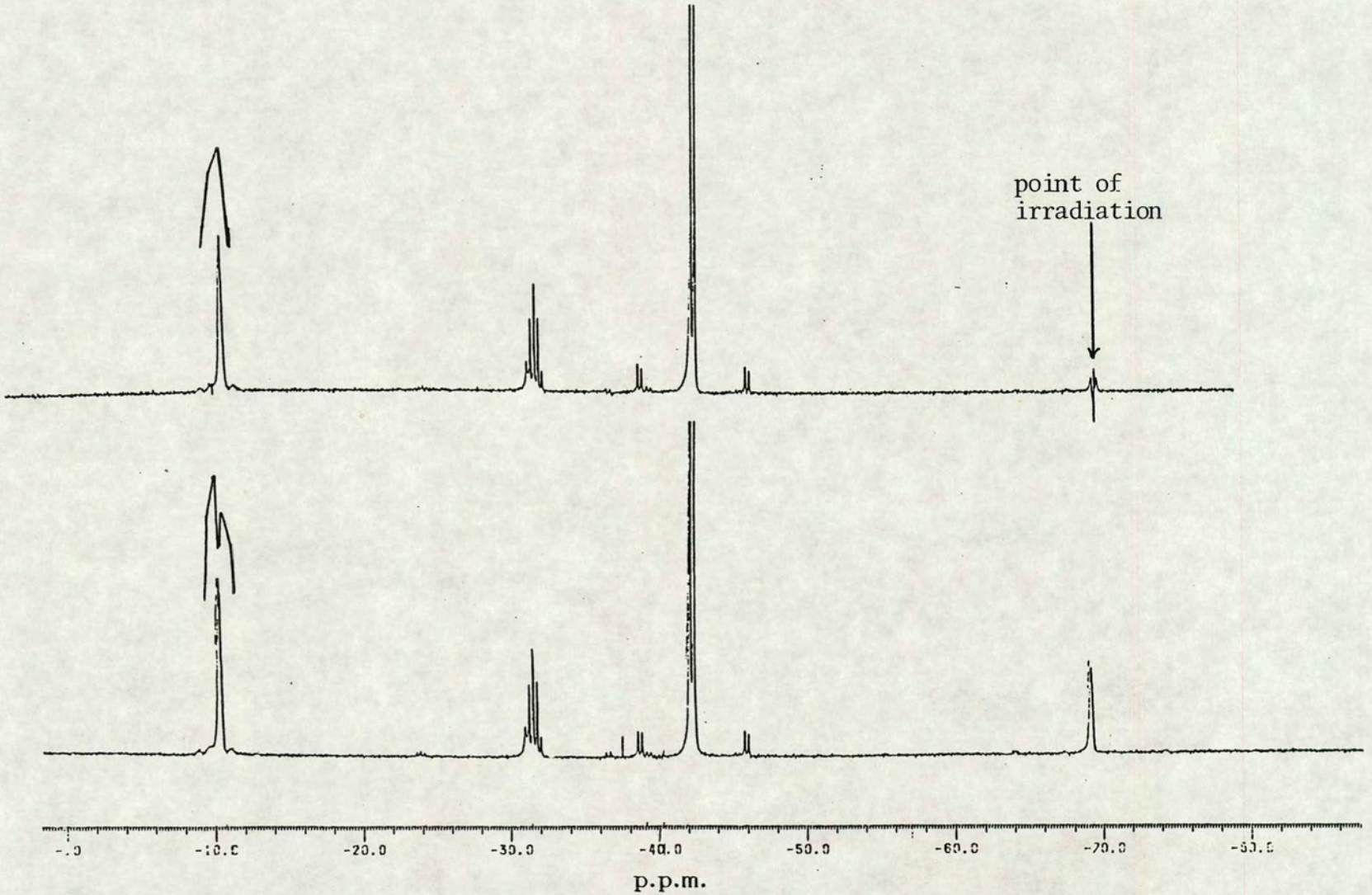


Figure 5.1.13; ^{19}F-^{19}F COSY n.m.r. spectrum of $Rh(CO)Cl(PEt_3)_2 + TeF_4$

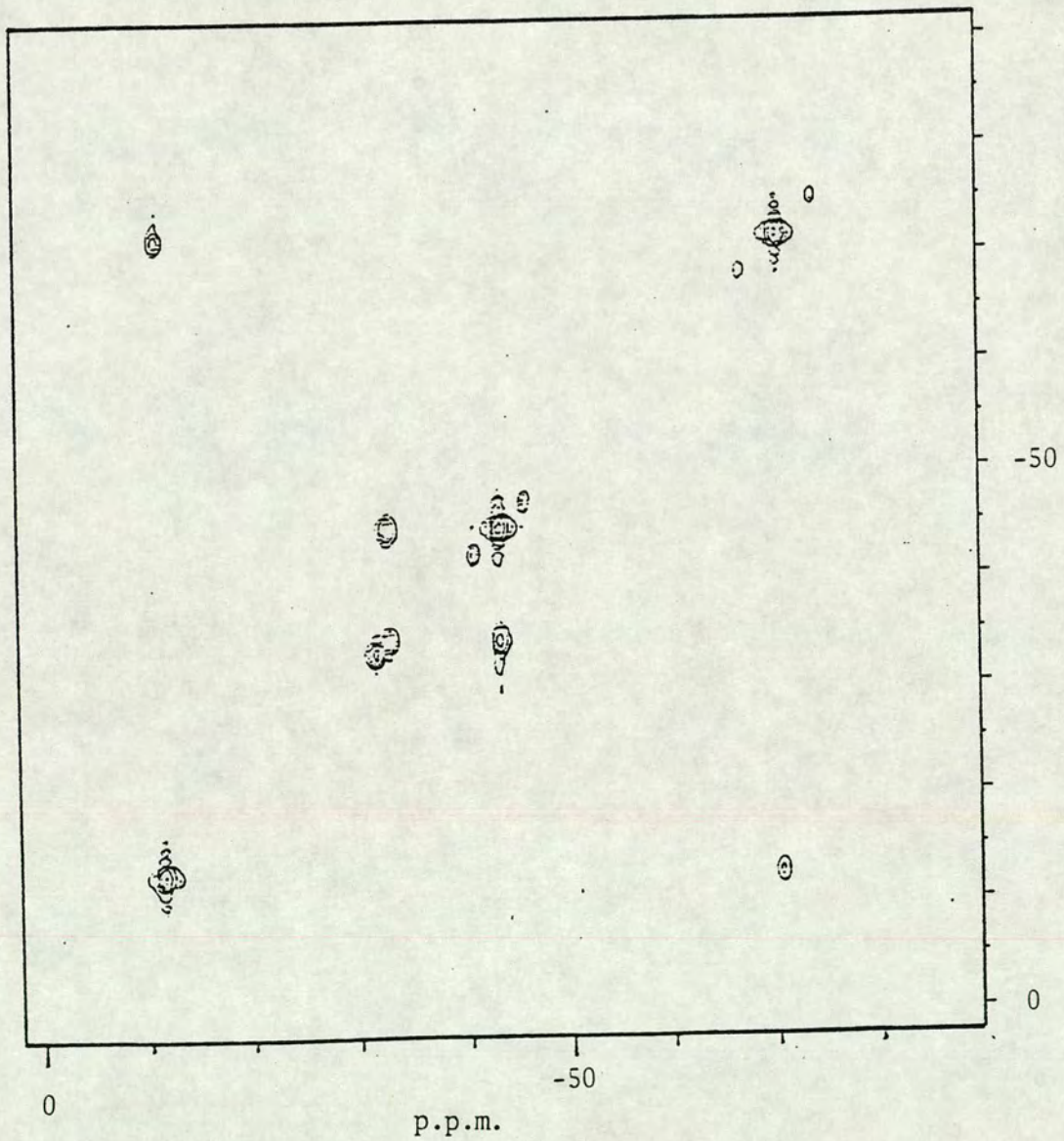
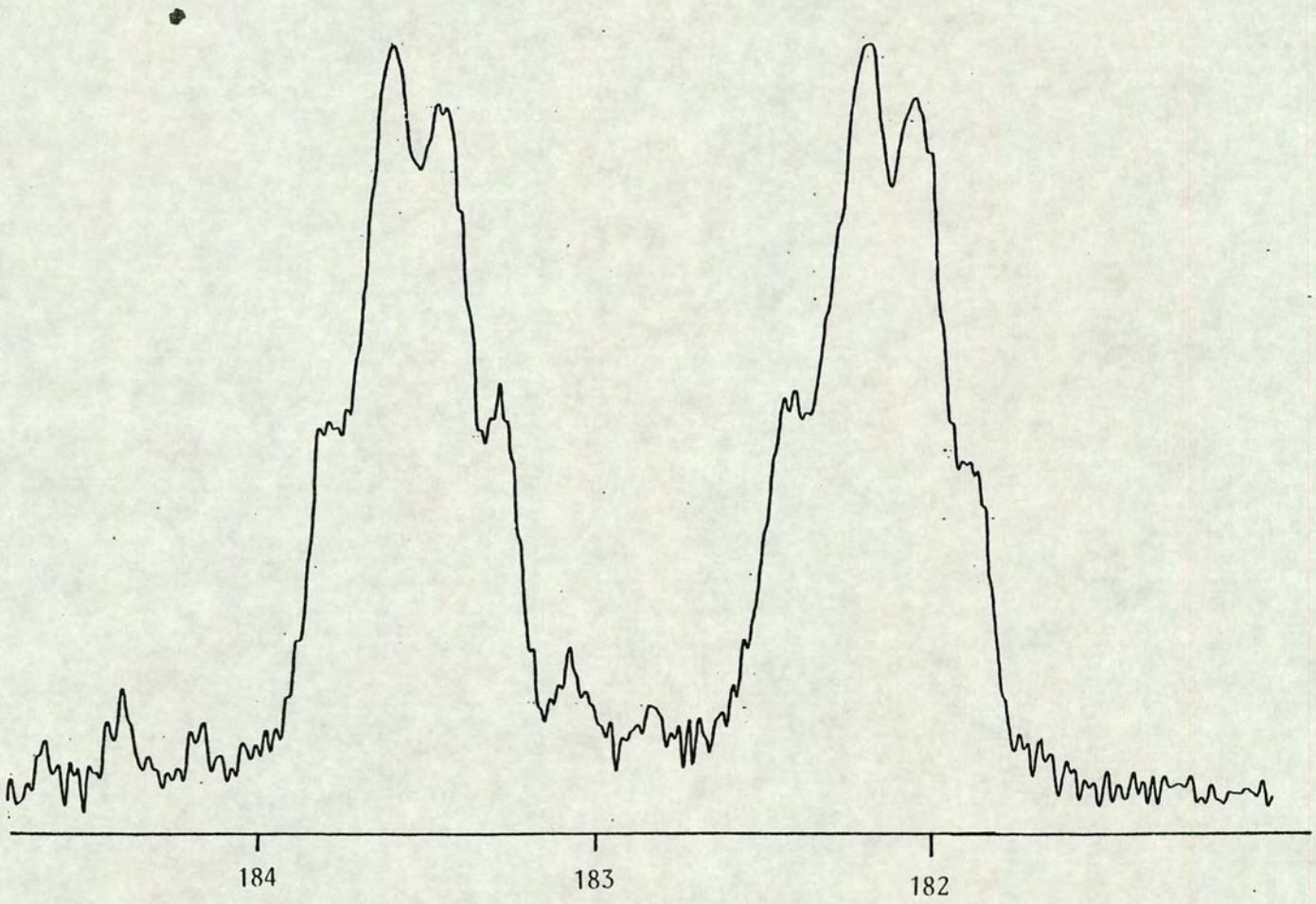


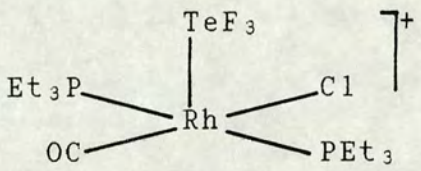
Figure 5.1.14; $^{13}C-\{^{1}H\}$ n.m.r. spectrum of $Rh(CO)Cl(PEt_3)_2 + TeF_4$



coupling to fluorine is only a doublet and not a triplet this carbonyl group must be coupling to the equatorial Te-F and, indeed, on observation of the $^{19}F-\{^{1}H\}$ n.m.r. spectrum of this complex we did observe a clear doublet coupling of 8Hz.

All of the evidence we have is consistent with our assignment of a five coordinate square pyramidal complex [XXXIX].

[figure 5.1.15]



[XXXIX]

Chem. Shift/p.p.m.	Coupling Const./Hz				
δ_{F1} = -9.6	$^{2}J_{F1-F4}$ = 23	$^{1}J_{F4-Te}$ = 1920
δ_{F4} = -68.4	$^{2}J_{F1-Rh}$ = 18	$^{3}J_{F4-P}$ = 4
δ_{P} = 27.4	$^{3}J_{F1-P}$ = 16	$^{3}J_{F4-C}$ = 8
δ_{C} = 182.7	$^{1}J_{F1-Te}$ = 266	$^{2}J_{P-C}$ = 9
	$^{1}J_{P-Rh}$ = 92	

On observing the $^{19}F-\{^{1}H\}$ n.m.r. spectrum at 235K both TeF_5^- resonances began to lose their couplings and at 255K both resonances had lost their coupling to each other. The two Rh-TeF_3 resonances remained unchanged at this temperature. At 263K the TeF_5^- resonances had begun to broaden and coalesce and at 275K one broad, unresolved resonance was observed at δ-39.3 indicating that all five fluorines of the TeF_5^- group

were equivalent on the n.m.r. timescale. On further warming to 313K, no further change was observed in the ^{19}F n.m.r. spectrum. On recooling to 195K from this temperature, the original four resonances were again observed indicating that the Rh-TeF_3 complex was stable to higher temperature than the Rh-SF_3 or Rh-SeF_3 complexes discussed in this thesis and that the exchange which occurred in the TeF_5^- group was fully reversible.

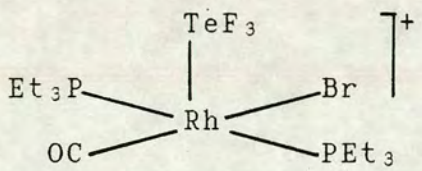
5.2 Reaction of $Rh(CO)Br(PEt_3)_2$ with TeF_4.

At 195K the $^{19}F-\{^1H\}$ n.m.r. spectrum showed four resonances F_1, F_2, F_3, and F_4 at δ-6.8, δ-30.8, δ-42.2 and δ-65.0 of approximate ratios 2:1:4:1 respectively [figure 5.2.2]. As in the previous reaction, all four resonances showed coupling to ^{125}Te, and the two resonances F_2 and F_3 were assigned as arising from the pentafluorotellurate(IV) anion.

The resonance at δ6.8 was a doublet of doublets of triplets and the resonance at δ-65.0 was again a triplet which showed signs of other couplings which were difficult to resolve.

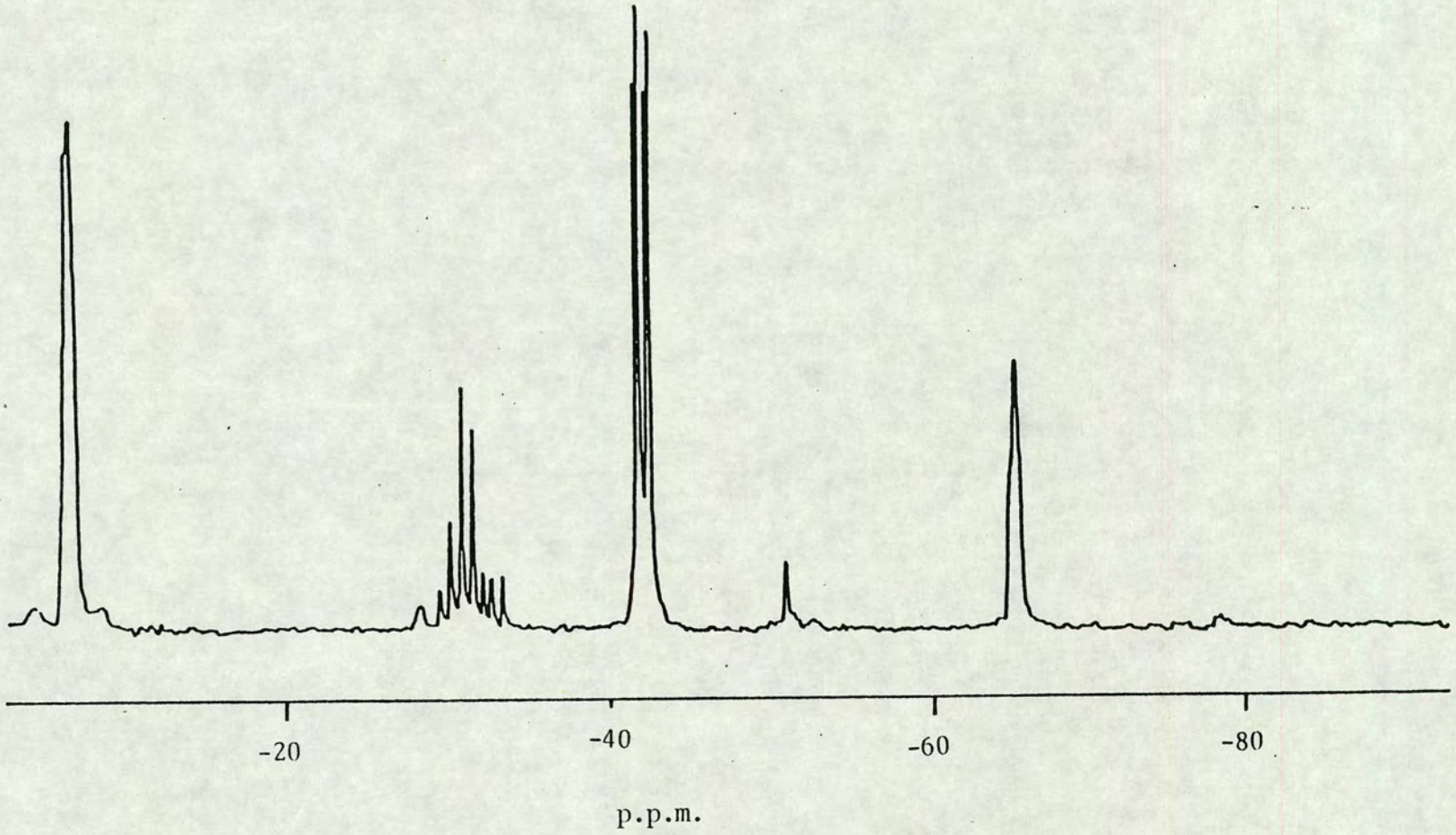
The $^{31}P-\{^1H\}$ n.m.r. spectrum at 195K showed a doublet of triplets of doublets at δ25.1. $^1J_{P-Rh}$ was 92Hz which again suggested a five coordinate complex, as did the ^{13}C n.m.r. spectrum which showed a doublet of triplets of doublets at δ182.0. On the basis of these chemical shifts and coupling constants and by analogy with reaction 5.1 we have assigned these n.m.r. data as arising from complex [XL];

[figure 5.2.1]



[XL]

Figure 5.2.2; $^{19}F-\{^{1}H\}$ n.m.r. spectrum of $Rh(CO)Br(PEt_3)_2 + TeF_4$



Chem. Shift/p.p.m.	Coupling Const./Hz				
δ_{F1} = -6.8	$^2J_{F1-F4}$ = 22	$^1J_{F4-Te}$ = 1900
δ_{F4} = -65.0	$^2J_{F1-Rh}$ = 16	$^3J_{F4-P}$ = 3
δ_{P} = 25.1	$^3J_{F1-P}$ = 16	$^3J_{F4-C}$ = 9
δ_{C} = 180.9	$^1J_{F1-Te}$ = 280	$^2J_{P-C}$ = 10
	$^1J_{P-Rh}$ = 92	

On warming, no change was observed in the resonances arising from the TeF_3 group but the two resonances assigned to the TeF_5^- anion began to lose their coupling at 225K and had coalesced to a broad lump at 240K. No further change was observed on warming and on recooling to 195K from 315K the original spectrum was again observed.

Since the TeF_5^- anion undergoes an exchange process at 240K in this system compared to 275K in the analogous chloride reaction and the only difference between these reactions is, apparently, the presence of different Rh-TeF_3 complexes. we may assume that these rhodium complexes must influence the behaviour of the TeF_5^- ions. This, therefore provides us with some evidence that is consistent with our earlier suggestion that we have 5 coordinate rhodium complexes with, perhaps, the sixth coordination site being filled by one of the fluorines of a TeF_5^- anion.

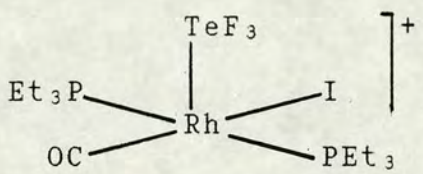
5.3 Reaction of $Rh(CO)I(PEt_3)_2$ with TeF_4.

At 195K several resonances were observed in the $^{19}F-\{^1H\}$ n.m.r spectrum [figure 5.3.2]. The most intense were the two resonances arising from TeF_5^-. Also observed were several weak, unresolved resonances in the region associated with F bonded to Te(IV) which we were unable to assign, as well as two relatively intense resonances at δ-152 and δ-180 which were characteristic of SiF_4 and HF. The SiF_4 is present as a result of HF attack on glass and the HF is likely present as a decomposition product.

On warming to 210K the weak TeF resonances disappeared and did not reappear on recooling, indicating decomposition.

We are, therefore, unable to be certain whether a complex of the form;

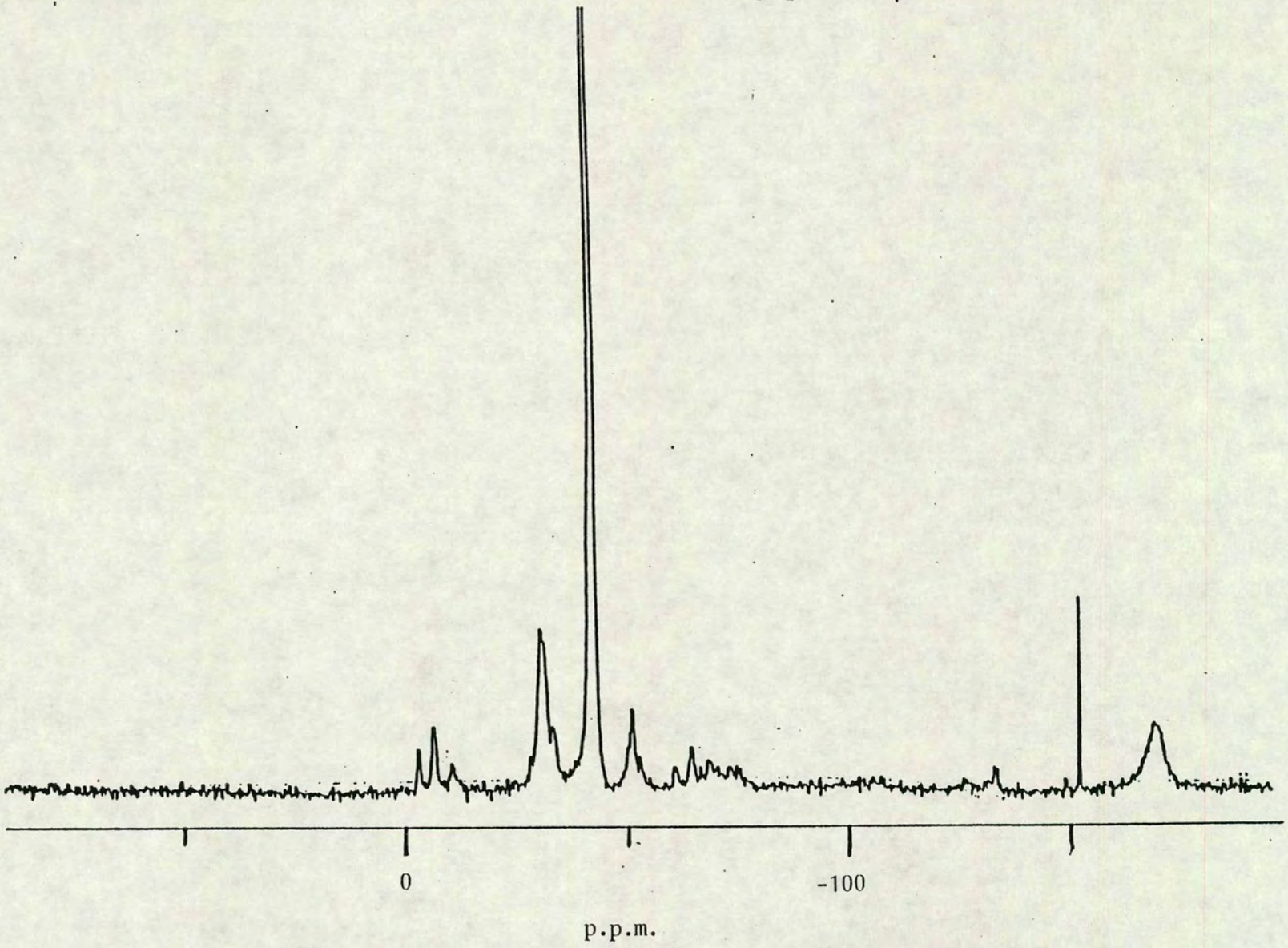
[figure 5.3.1]



[XLI]

was formed and subsequently decomposed at this temperature or whether TeF_4 reacted with $Rh(CO)I(PEt_3)_2$ in a different manner to the analogous chloride and bromide complexes. Whatever the answer, any rhodium complex containing tellurium fluorides was unstable.

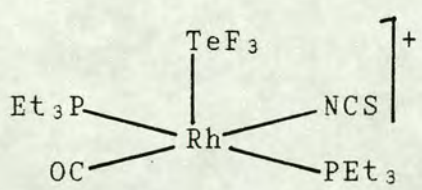
Figure 5.3.2; $^{19}F-\{^{1}H\}$ n.m.r. spectrum of $Rh(CO)I(PEt_3)_2 + TeF_4$



5.4 Reaction of $Rh(CO)NCS(PEt_3)_2$ with TeF_4

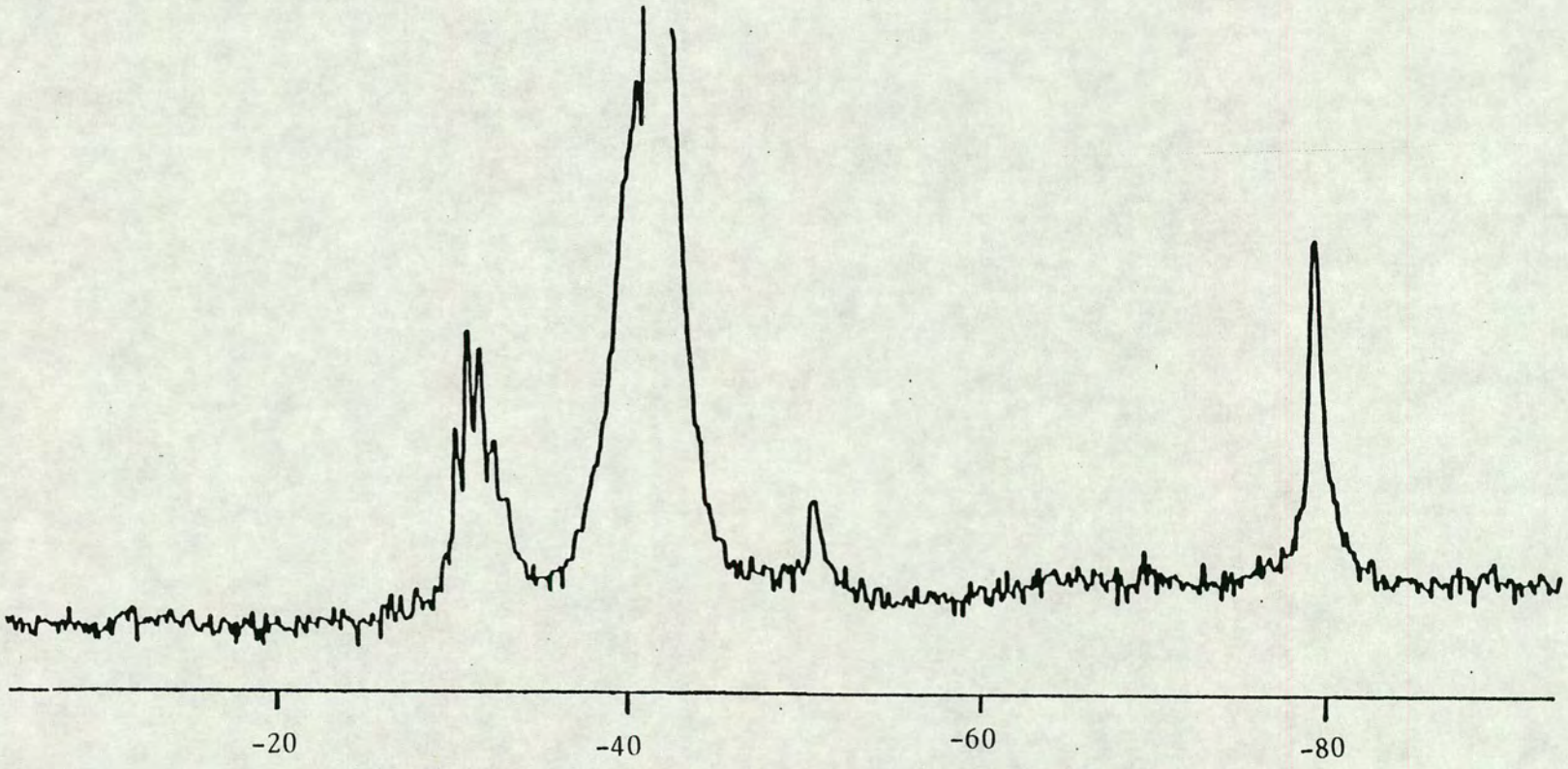
At 195K the $^{19}F-\{^1H\}$ n.m.r. spectrum showed three resonances, F_1, F_2 and F_3 at δ-30.8, δ-41.7 and δ-79.5 the ratios of which were approximately 1:6:1 [figure 5.4.1]. The two resonances at δ-30.8 and δ-41.7 were assigned to TeF_5^-. The resonance arising from the equatorial fluorines of TeF_5^- had a shoulder on the high frequency side which we believe may be due to two axial Te-F's of a TeF_3 group, on the basis of the integrals and also since the resonance at δ-79.5 had ^{125}Te satellites whose coupling to fluorine was of the same order as those observed in the Rh-TeF_3 complexes of the analogous chloride and bromide systems. Unfortunately this resonance could not be resolved and so no information could be deduced from coupling constants. It is possible that observation of the ^{19}F n.m.r. spectrum of this reaction at higher field would spread the spectrum out so that no resonances were overlapping.

The $^{31}P-\{^1H\}$ n.m.r. spectrum at 195K was rather broad and unresolved although $^1J_{P-Rh}$ was observed to be 94Hz which was of the same order as those previously assigned to square pyramidal TeF_3 complexes of rhodium. On the basis of these few results we have tentatively assigned these spectra as arising from complex [XLII]; [figure 5.4.1]



[XLII]

Figure 5.4.2; $^{19}F-\{^{1}H\}$ n.m.r. spectrum of $Rh(CO)NCS(PEt_3)_2 + TeF_4$



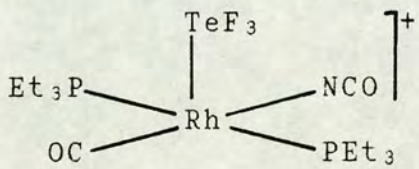
On warming, no change was observed in the $^{19}F-\{^{1}H\}$ n.m.r. spectrum until 240K when the two TeF_5^- resonances began to lose their coupling to each other and at 250K the coupling had disappeared and both resonances began to broaden. At 265K only one broad resonance was observed at δ-38.9 due to exchange of the fluorines in TeF_5^-. However, no change was observed in the resonance at δ-79.5 on warming up to 310K, indicating that if this resonance does arise from complex [XLII] then it does not decompose at ambient temperature.

5.5 Reaction of $Rh(CO)NCO(PEt_3)_2$ with TeF_4.

The $^{19}F-\{^1H\}$ n.m.r. spectrum at 195K was very similar to that observed in the reactions of TeF_4 with $Rh(CO)Cl(PEt_3)_2$ and $Rh(CO)Br(PEt_3)_2$. Four resonances, F_1, F_2, F_3 and F_4 were observed at δ-14.7, δ-30.7, δ-42.3 and δ-70.5 whose intensities were approximately 2:1:4:1 respectively [figure 5.5.2]. F_2 and F_3 were again assigned as arising from the pentafluorotellurate(IV) anion but the other two resonances would not resolve.

The $^{31}P-\{^1H\}$ n.m.r. spectrum at 195K showed a rather broad doublet of triplets at δ27.8 ($^1J_{P-Rh}$ = 94Hz, $^2J_{P-F}$ = 12Hz). By analogy with the analogous chloride and bromide reactions we have, again only tentatively, assigned these n.m.r. data as having arisen from complex [XLIII];

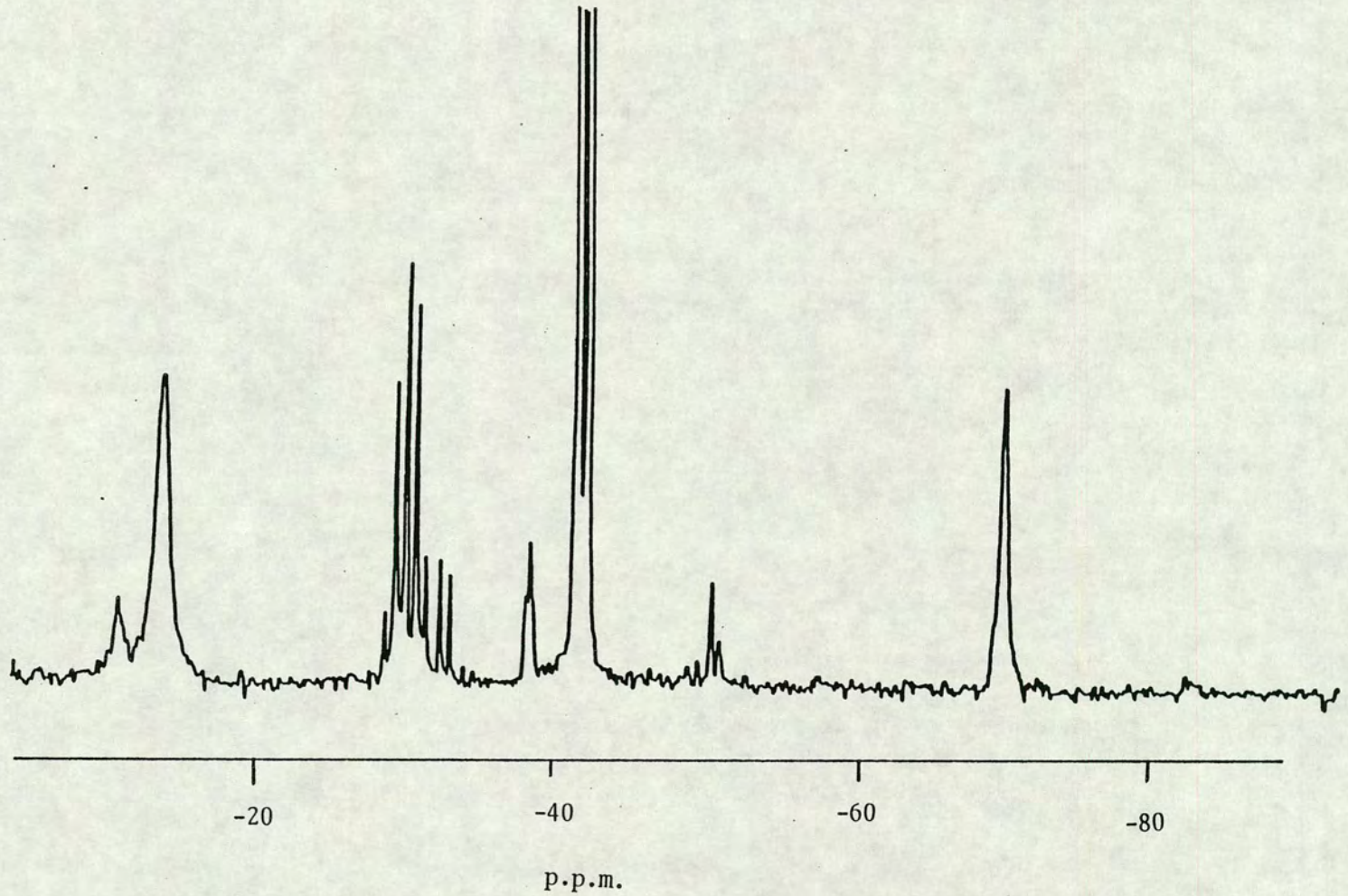
[figure 5.5.1]



[XLIII]

On warming, all four resonances began to broaden at 215K and at 220K the two resonances assigned as arising from the TeF_3 group had disappeared and did not reappear on recooling to 195K indicating decomposition. The characteristic resonances of SiF_4 and HF appeared at this temperature. On further warming to 230K the two TeF_5^- resonances had coalesced to a broad resonance at δ-39.0.

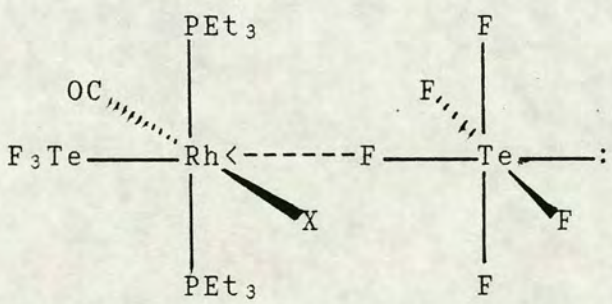
Figure 5.5.2; $^{19}F-\{^{1}H\}$ n.m.r. spectrum of $Rh(CO)NCO(PEt_3)_2 + TeF_4$



5.6 Discussion.

Unlike the analogous reactions of SF_4 and SeF_4 we are unable to fully assign the products of reaction of TeF_4 with $Rh(CO)X(PEt_3)_2$ [X = Cl, Br, I, NCS, NCO]. However, all of the evidence seems to suggest that, TeF_4, like SF_4 and SeF_4, undergoes oxidative addition to the rhodium(I) complexes. For X = Cl, Br and NCO, and probably NCS, we observe very similar spectra suggesting similar complexes. The only difference is the halide, or pseudohalide. From the magnitude of $^1J_{P-Rh}$ we have assigned the geometry at rhodium to be square pyramidal and from the fact that the fluxionality of the TeF_5^- group varies with X we believe that the pentafluorotellurate(IV) anion may interact with the vacant coordination site on rhodium to give a pseudooctahedral complex;

[figure 5.6.1]



The only way, however, to be certain of the geometry of these species will be to obtain an x-ray crystal structure. We attempted many times to grow single crystals of these complexes, and succeeded on several occasions, but the sensitivity of the solutions to air and moisture has made obtaining a structure

impossible to date.

We have observed no fluorine nuclei directly bonded to rhodium in any reactions with TeF_4, which is very different from our observations in the analogous sulphur and selenium reactions. This result, however, is not surprising since we observed that raising the temperature of certain Rh-SeF_3 complexes resulted in an increase in the reactivity of the Rh-F bond. It is not improbable that in the analogous tellurium system the Rh-F bond is so reactive that it reacts immediately it is formed. This increased reactivity could be a result of either of the two suggestions given for the reactivity of the Rh-F bond in SeF_3 complexes i.e. less electron withdrawal from rhodium by the more diffuse tellurium d-orbitals resulting in less π-donation to rhodium from the filled p-orbitals of the Rh-F or more steric interaction between the long Te-F bonds and the ethyl groups of the phosphines leading to less interaction with the Rh-F.

If our assignment of the n.m.r. data to these complexes is correct then we observe that these TeF_3 complexes are fluxional at even lower temperatures than their selenium analogues. This can also be explained using the same arguments that we used to explain why SeF_3 complexes were more fluxional than SF_3 complexes, namely poorer overlap of the empty $d\pi$ orbitals of tellurium with the filled $d\pi$ orbitals of rhodium than with sulphur or selenium.

We have discussed in the introduction to this

thesis that the pentafluoro complex ions of sulphur, selenium and tellurium are all known but that they are not usually formed from the tetrafluorides. There is one report by Asprey et. al.[77] that the reaction of TeF_4 with $(Bu_2NH_2)F$ in methylene chloride solution produced a mixture of TeF_5^- and TeF_6^{2-}. However, their assignment of these ions is based purely upon ^{19}F n.m.r. chemical shifts as no couplings were observed in either resonance. As we believe that TeF_4 has either abstracted a fluoride ion from a six coordinate complex or "mopped-up" the free fluoride ion from solution we performed a simple experiment in an attempt to discover how good a fluoride acceptor TeF_4 is. TeF_4 was added to a mixture of simple 6 coordinate Rh(III)-F complexes prepared by reacting $Rh(CO)Cl(PEt_3)_2$ with XeF_2 in methylene chloride. The resulting $^{19}F-\{^1H\}$ n.m.r. spectrum showed very intense resonances arising from TeF_5^- with the expected F-F couplings. This proves that TeF_4 is a relatively good fluoride acceptor and provides yet further support for our assignments of the Rh-TeF_3 complexes discussed in this chapter.

Chapter Six.

Vacuum Line Techniques

With the exception of SeF_4, all volatile compounds were handled on a pyrex vacuum line of conventional design[78]. The line was built from detachable sections joined by ground glass joints to facilitate cleaning and Apiezon L & N greases were used on joints and taps respectively [Fig. 6.1.1].

Detachable ampoules were fitted with Sovirel greaseless taps. Schlenk tubes were attached to the line via cone-to-cone tap adaptors. The vacuum was maintained by a 3-stage mercury diffusion pump assisted by a rotary oil pump [Model ED50, Edwards High Vacuum Ltd., Crawley, Sussex].

Pressure of non-condensible gas in the vacuum line was checked by a Pirani gauge. The pressure of gases in the sections of the line were measured using a spiral gauge with mirror, used as a null point device with a lamp and scale. The volume of the line was calculated using a molecular weight bulb. Accurate volumes for individual sections combined with pressure readings allowed accurate measurements of volatile materials.

SeF_4 was handled on a nickel-steel manifold of conventional design with high and low vacuum facilities [79]. This was constructed from 3/8" o.d., 1/8" i.d. 316 stainless steel tubing [George Mellor Ltd., Ealing, London] and a stainless steel "U" trap (25cm^3 capacity). The manifold was completed with AE-30 series hard drawn stainless steel needle valves, crosses and "T"s

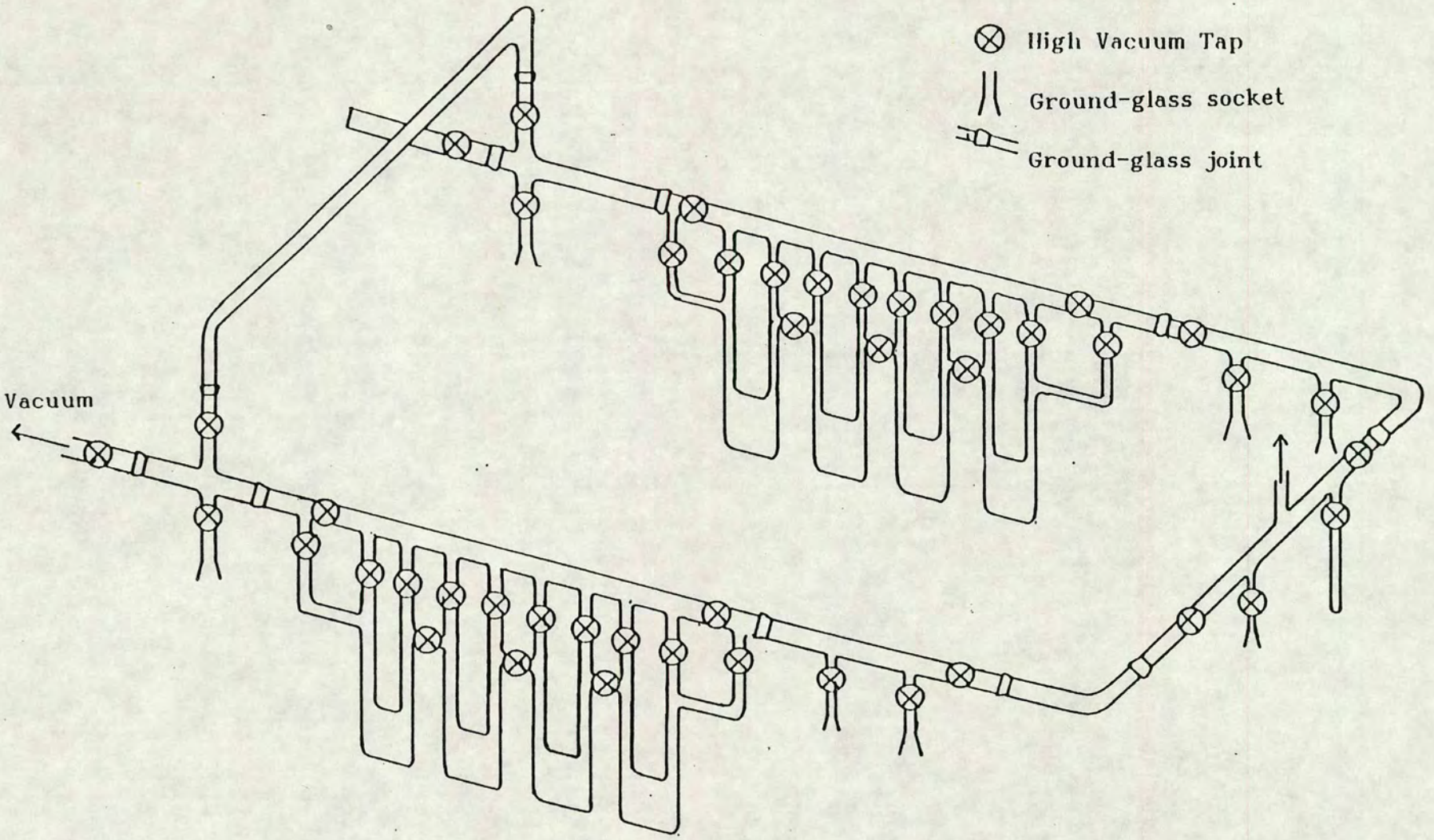
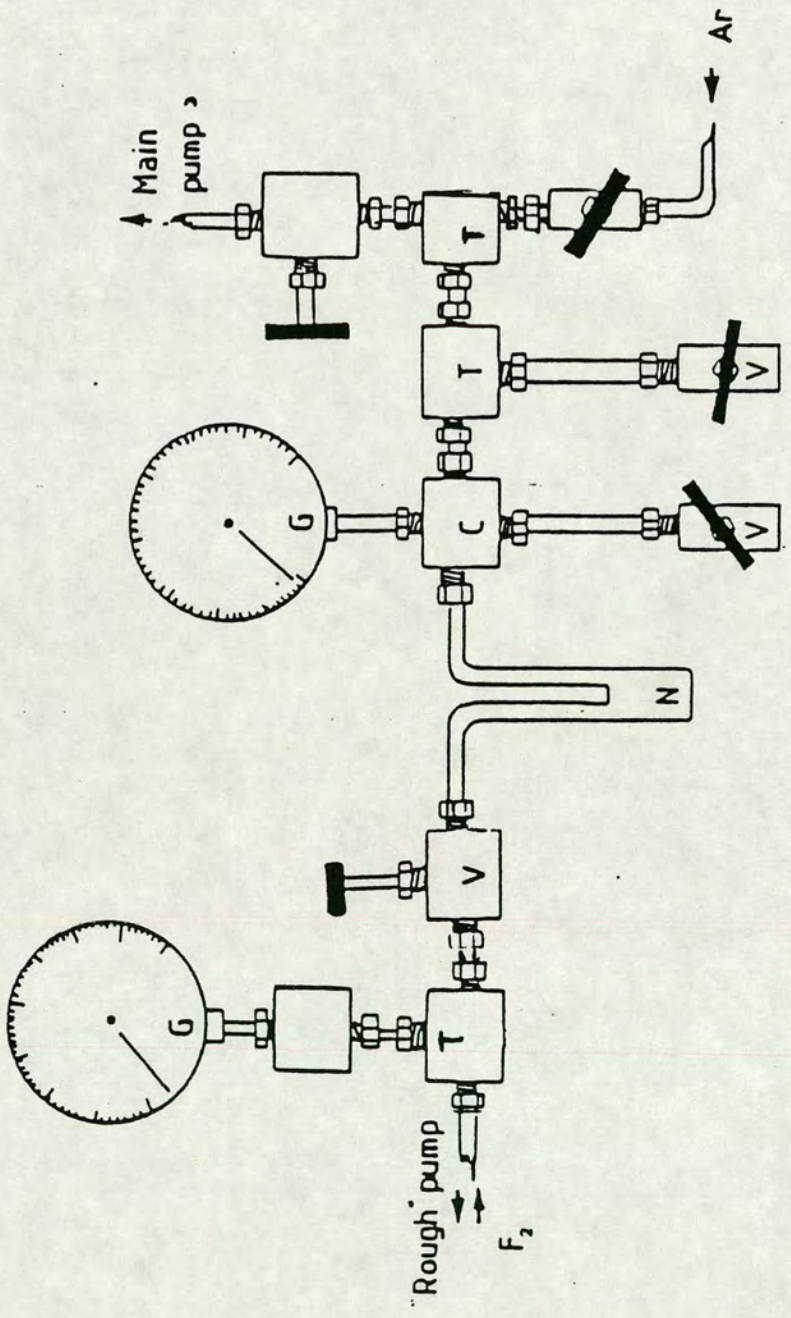

High Vacuum Tap
Ground-glass socket
Ground-glass joint
Vacuum

Figure 6.1.1.

[Autoclave Engineers Inc., Erie, Pennsylvania, USA] [Fig. 6.1.2]. The low vacuum system (10^{-2} mmHg) consisted of a single-stage rotary pump [Model ED50, Edwards] with a large metal trap charged with soda lime granules (5-10 mesh) between the pump and the manifold. The function of the chemical trap was to remove fluorine and volatile fluorides from the manifold. The low vacuum system served to remove large volumes of gases before opening the manifold to the high vacuum system. The main system vacuum (10^{-5} mmHg) was maintained by a single stage rotary pump [Model ED50, Edwards], standard triple stage mercury diffusion pump and -196°C cold trap. Facilities for admission of dinitrogen directly into the manifold from cylinders were provided and sulphur tetrafluoride or fluorine for seasoning the apparatus was introduced to the line from welded nickel cans (1 dm^3 capacity) fitted with AE-30 stainless steel needle valves. Manifold pressures of plus or minus one atmosphere (0-1500 mmHg ±5 mm Hg) were measured using a stainless steel Bourdon-tube gauge [Type 1F/66Z, Budenberg Gauge Co. Ltd., Broadheath, Greater Manchester]. The vacuum was monitored using a Pirani gauge. A variety of Pyrex, metal or fluoroplastic reaction vessels could be attached to the vacuum line. Glass systems were attached to the manifold via 1/4" o.d. glass connected to 1/4" o.d. stainless steel tubing (manifold outlet) with ChemCon Teflon connectors [Type STD/4 E1P, Production Techniques Ltd., Fleet, Hampshire]

Figure 6.1.2



C - Stainless steel cross
G - Bourdon tube gauge
N - Nickel "U" trap
T - Stainless steel "T"
V - Stainless steel needle valve

using Teflon compression unions. Small fluoroplastic reactors were fabricated by heating and moulding either 6mm o.d. or 4mm o.d. Kel-F tubing [Voltalef, Paris]. These reactors were fitted with ChemCon Teflon needle valves by 1/4" o.d. compression unions.

Handling of Air-Sensitive Solids

Air-sensitive solids were prepared and handled on a Schlenk vacuum and nitrogen line[77] using high purity dinitrogen (B.O.C. white spot specified less than 0.5% H_2O and O_2). Preparations were carried out in pyrex reaction vessels with tapped side-arms to allow evacuation, evaporation of solvents and addition of dinitrogen. Reactions were agitated with teflon coated stirrer bars.

Reactions in Sealed N.M.R. Tubes

Most of the reactions discussed in this thesis were carried out in sealed n.m.r. tubes in order to observe the reactions as they took place.

In a typical reaction 0.1 mmole of metal complex was weighed into an n.m.r. tube with a B10 cone attached. The tube was evacuated and deuterated solvent was distilled in to a depth of ca. 3 cm. The complex was then dissolved by warming the tube to ambient temperature. The required amount of volatile reactant was then condensed into the tube, which was sealed and stored at liquid nitrogen temperature. Spectra were then recorded at the desired temperature. In some cases where

HF was assumed to be present, CsF was added simultaneously with the metal substrate, to "mop-up" the HF.

For reactions involving SeF_4, F.E.P. tubing (4mm. o.d., 3mm i.d.) was used instead of n.m.r. tubes as SeF_4 reacts with glass. The SeF_4 was condensed into the F.E.P. tube as in the case of the volatile gases and the tube was sealed off by a heating coil and kept at liquid nitrogen temperature.

N.m.r. spectra of these tubes were observed by inserting the tube into a shortened n.m.r. tube containing ca. 1cm of d-6 acetone, kept rigid by a tight-fitting cap and run in the normal way by locking on to the d-6 acetone [Fig 6.1.3]. For reactions involving TeF_4, this was weighed into the n.m.r. tube first, inside a dry box and the metal substrate was added afterwards at liquid nitrogen temperature under a stream of dinitrogen.

Solvents

Solvents were purified as follows:

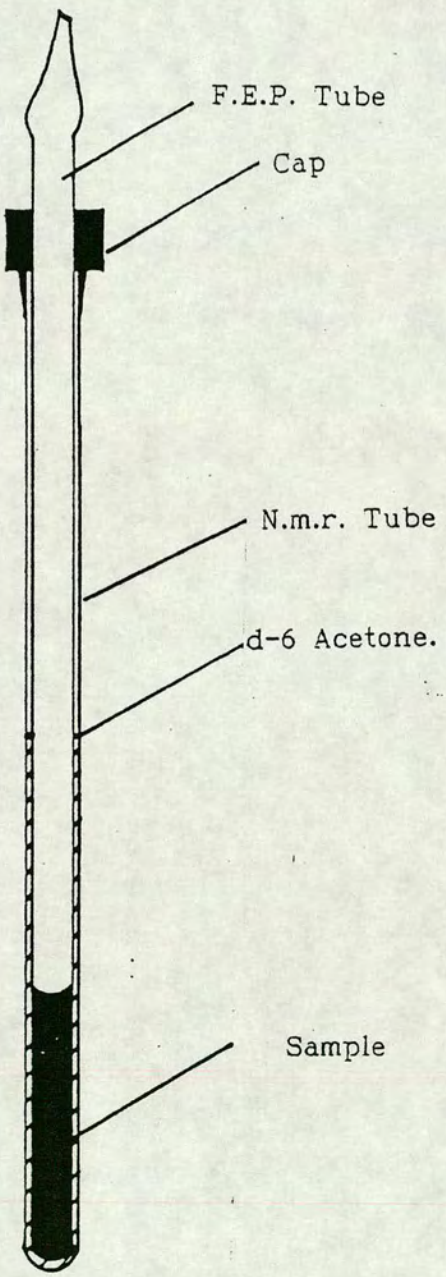
CH_2Cl_2 - commercial grade, predried over $CaCl_2$, distilled from $CaSO_4$ and stored over roasted 4A molecular sieve.

$(CH_3)_2O$ - commercial grade, dried over roasted 4A molecular sieve.

Et_2O - commercial grade , dried over sodium wire.

Toluene - commercial grade, dried by distillation from CaH_2.

Figure 6.1.3.



N.m.r. solvents were stored over roasted 4A molecular sieve and distilled prior to use.

N.m.r. Spectrometers

Variable temperature n.m.r. spectra were recorded on the following fourier-transform spectrometers;

Jeol FX60Q,	^{31}P
Jeol FX90Q,	^{31}P
Bruker WP80,	^{19}F
Bruker WP200,	^{13}C, ^{19}F, $^{19}F-\{^{19}F\}$, ^{31}P
Bruker AM300,	^{19}F, $^{19}F-^{19}F$ COSY
Bruker WH360,	^{13}C, ^{31}P

Vibrational Spectra

All volatile reagents were checked for purity by i.r. spectroscopy on a Perkin-Elmer 598 double-beam spectrometer in an i.r. cell fitted with KBr windows. Metal substrates were checked by running nujol mulls between KBr plates [table 5.1]

SeF_4 purity was checked by running the Raman spectrum on a Spex Ramalab Raman spectrometer.

Preparation of SF_4[23]

NaF (210g) was added to 800ml of dried CH_3CN in a 2L.3-necked round-bottomed flask and stirred gently. SCl_2 (160ml) was added slowly (1 hour) and then under a minimum flow of dinitrogen, the mixture was warmed to

50°C for 1 hour. The temperature was then raised to 70°C for 1 further hour and crude product and CH_3CN collected in a -78°C trap. The trap was then connected to the vacuum line and cooled to -78°C and the volatiles collected at this temperature. The CH_3CN was removed by repeated fractionation through -78°C. The resultant yellow liquid was a mixture of SF_4, SOF_2 and Cl_2.

The SF_4 was purified by cocondensing equal amounts of the above and BF_3 into a 1L flamed Sovirel bulb. This was warmed to room temperature, cooled to -78°C and the volatiles (SOF_2 & Cl_2) pumped away. 0.5 equivalents of diethyl ether was then condensed into the bulb which was again warmed to room temperature and recooled to -78°C, then, pure SF_4 was pumped off.

Preparation of BF_3[81]

NaF (10g) and anhydrous B_2O_3 (1.7g) were ground together and placed in a 500ml. three-necked round bottomed flask. Conc. H_2SO_4 (11ml) was added and the flask was then connected to a pyrex vacuum line via a cold-finger condenser cooled to -78°C. The flask was then heated with a cool flame and BF_3 was collected in traps held at -196°C. The BF_3 so obtained was purified by fractionating through -160°C bath (isopentane/liq. N_2) into a -196°C trap.

Preparation of SeF_4[31]

SeO_2 (2.2g) was placed in a 20ml stainless steel Hoke pressure vessel. The vessel was connected to a metal vacuum line and evacuated and cooled to -196°C.

SF_4 (6.5g) was condensed into the vessel which was then sealed and heated to 120°C for 12 hours with stirring of the reaction mixture. After cooling to ambient temperature the vessel was further cooled to -196°C. The products were then fractionated through traps held at -78 and -196°C. The pure product was then found in quantitative yield in the -78°C trap.

Preparation of TeF_4[36]

TeO_2 (2.0g) was placed in a 20ml stainless steel Hoke pressure vessel. The vessel was connected to a metal vacuum line and evacuated and cooled to -196°C. SF_4 (5.0g) was condensed into the vessel which was then sealed and heated to 130°C for 15 hours with stirring of the reaction mixture. After cooling to ambient temperature all the gaseous products were removed by pumping. The crystalline residue remaining in the pressure vessel was then transferred in a dry box to a glass sublimator. Sublimation at 100°C/10^{-2} torr afforded pure TeF_4.

Preparation of $Rh(CO)Cl(PEt_3)_2$[82]

1 gram of $RhCl_3.3H_2O$ was dissolved in MeOH (9.6ml) and EtOH(9.6ml) and 1.17ml PEt_3 added. 11.5ml of N KOH(aq.) was added and the mixture refluxed under a flow of dinitrogen for 2 hours. The mixture was then allowed to cool to ambient temperature and 1.1ml of concentrated HCl was added to neutralise the solution. Then the solid was filtered off, dried under vacuum for 1 hour and then sublimed on to a cold finger (p = $10^{-2}\tau$,

T = 105°C) as a yellow solid.

Preparation of $Rh(CO)X(PEt_3)_2$ [X = Br, I, SCN, OCN][83,84]

All of these complexes were prepared by metathesis of $Rh(CO)Cl(PEt_3)_2$ with the relevant alkali metal halide or pseudohalide in degassed acetone;

X	MX	Stir Time	Purification
Br	LiBr	1 hour	Sublimation
I	NaI	15 mins.	Sublimation
SCN	NaSCN	1 hour	Extraction with CH_2Cl_2/Et_2O
OCN	KOCN	2 Hours	Extraction with CH_2Cl_2/Et_2O

XeF_2[85] kindly supplied by Dr. M. J. Rieland.

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